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A MANUAL

OF

ANALYTICAL CHEMISTRY.

BY

HENRY ROSE,

PROFESSOR OF CHEMISTRY AT BERLIN.

TRANSLATED FROM THE GERMAN

BY

JOHN GRIFFIN.

LONDON:
PRINTED FOR THOMAS TEGG, 73, CHEAPSIDE:
J. CUMMING, DUBLIN;
AND R. GRIFFIN AND CO. GLASGOW.

1831.

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TRANSLATOR'S PREFACE.

The high repute in which the Author of the following Work is held as an Analyst, renders it altogether unnecessary for me to offer any apology for the publication of this Translation. As the English chemist possesses at present no competent literary instructor to guide him in his analytical researches, it may be presumed that a Work, emanating from the BERLIN SCHOOL, and sanctioned by the name of ROSE, will not be looked upon with indifference.

I have taken the utmost pains to ensure the accuracy of the Translation; but since perfect correctness is unattainable, it is possible that the reader may still sometimes find occasion to censure me for want of perspicuity. I trust, however, that this will not often be the case.

The original Work (*Handbuch der analytischen Chemie von* HEINRICH ROSE, Berlin) has been published about a year. I was in Germany at the time of its appearance, and commenced the translation immediately. My work has been ready for publication some time; but having, since my return to England, received a quantity of additional matter from Mr. Rose, I have translated and incorporated it in the seventh section of the First Part. This original matter was of considerable importance, comprehending not only a number of complete articles, but all that relates to the influence of organic substances upon the action of the different reagents. I take this opportunity of thanking Mr. Rose for the politeness which has afforded me the means of giving this additional value to the following pages.

With a view to facilitate reference, I have put head-lines to the pages; and have prefixed a short explanatory title to most of the paragraphs in Part II. These titles do not exist in the original Work, but I think they will be found useful. In some cases they do not describe the subject of the paragraphs with much precision; yet more precise titles would often have required a much greater number of words for their expression, and the present titles are sufficiently definite for most practical purposes.

In every other respect, the Translation is equivalent to the original Work. I have neither abridged nor enlarged it; not perceiving any thing that could be spared, nor caring to trouble the reader with questionable improvements. It is to be regretted that translators often permit themselves to be too much influenced by a zeal for reformation, and are consequently led to make additions and alterations where both are unnecessary. There be translations in which the Text "hides its diminished head" under the accumulated illustrations of the translator.

The Nomenclature of **Berzelius**, employed by **Rose** in the original Work, could not be employed by me with propriety. The theoretical ideas of **Berzelius** are far from being so generally known in this country as they deserve to be, and wherever his System is unknown, his names are unintelligible. I could have translated *Chlorammonium* by *Chloride of Ammonium*, but in that case, though the words would have been English, the sense would not; for it is by no means a common opinion among chemical students in England, that *Chloride of Ammonium* is synonymous with *Muriate of Ammonia.* The learned, indeed, would have understood the term, but I wish this book to have a wider sphere of action than that afforded by the closets of Professors. I have therefore rejected the Nomenclature of Berzelius, and employed the terms which are best understood among ourselves.

For nearly thirty years, scarcely a single German Chemical Work has been translated into English. I am quite unable to account for this circumstance. During the above period, the *Savans* of Germany have laboured with an industry and success, not at all surpassed, if even equalled, by that of the scientific men of Britain; and I could point out a variety of works, translations of which would form useful additions to our scientific literature. In Mineralogy, we have no work which is equal to the *Oryktognosie* of **Leonhard**; in Pharmacy, none that comes up to the *Pharmacie* of **Geiger**; and I will venture to affirm that the *Lehrbuch der Chemie* of **Berzelius**, and the *Handbuch* of LEOPOLD GMELIN are unequalled, both for quantity and quality of information, by any other chemical systems in existence. Yet these works are utterly disregarded by the majority of the chemists of this country. Without presuming to speculate on the causes of this apathy, I may indulge the hope that it will speedily pass away and be succeeded by a better spirit. Should the specimen of German science which I have the pleasure of introducing to British chemists, have the effect of turning their attention to the literature of the country whence it is derived, the circumstance will afford me much gratification.

LONDON, JANUARY, 1831.

AUTHOR'S PREFACE.

So different are the claims which can be made on a MANUAL OF ANALYTICAL CHEMISTRY, that it appeared to me to be difficult, in the execution of such a Work, to answer them all. I contented myself, therefore, with making it my principal aim to compose the Work in such a manner that those possessing sufficient knowledge of chemistry might employ it as a guide in analytical inquiries.

The First Part contains instructions on qualitative chemical examinations. I have treated therein of the detection of those substances only which occur most frequently. I have restricted myself thus, not only because these substances are of greater interest than those which seldomer occur, but especially because the description of the analyses would have been rendered too difficult to follow, had I started with the supposition that the compounds to be examined could contain all possible constituents. The behaviour of rare substances with reagents is described in the systems of chemistry, among others, in the system published by **Berzelius**. Every one, therefore, who is sufficiently exercised in the qualitative examination of the substances which commonly occur, will experience no difficulty in detecting those which seldomer occur, providing his inquiries are directed by the information thus obtained.

The Second Part contains instructions for quantitative analysis. To every simple substance, oxygen excepted, a distinct section is allotted. In each section, I first describe the quantitative determination of the simple substance and its compounds with oxygen: I then treat of the separation of this substance or its oxides from those which are treated of in every preceding section. In the beginning, come the simple bodies which, combined with oxygen, constitute *bases*; then follow the bodies whose compounds possess *acid* properties. This order appeared to me to be the most advisable, since it permits one to trace, without much difficulty, the particular steps of a process chosen for any quantitative analysis which may be presented. Only in a few places, and then but to avoid repetition, have I departed from this arrangement. By following this plan, it has been rendered possible to treat of the siliceous substances which occur in nature under silica, of the simple and compound, factitious or native sulphurets under sulphur, and of nearly all the gases under hydrogen.

In order still farther to facilitate reference, an Index has been added to the Work.

The description of the practical contrivances employed in Analytical Chemistry, is almost entirely passed over. For the introduction of most of these contrivances, and for the greatest improvements they have received, we are indebted to Berzelius. He has accurately described them in the Fourth Part of his System of Chemistry, with the translation of which *(into German)* Professor Wöhler is now occupied. It appeared to me, therefore, to be unnecessary to describe them in this Manual. In a few places only have I depicted by wood cuts some apparatus employed in quantitative analyses.

The chemical Nomenclature is precisely the same as that employed by **Berzelius** in his System of Chemistry.

Berlin, August, 1829.

CONTENTS.

PART I.

QUALITATIVE ANALYSIS.

SECTION I.

Page

INSTRUCTIONS for the qualitative examination of compounds which are soluble in water, and which consist only of a Base combined with an Acid, or of a Metal combined with a Non-metallic body; the constituents of such compounds not belonging to those which seldom occur, but being among those of which a list is subjoined 5

SECTION II.

Instructions for the qualitative examination of compounds which are either quite insoluble, or very sparingly soluble, in water, which however are soluble in muriatic or nitric acid, and which consist only of a Base combined with an Acid, or of a Metal combined with a Non-metallic body; the constituents of such compounds being among those before-mentioned 13

SECTION III.

Instructions for the qualitative examination of compounds which, both in water and in acids, are either quite insoluble, or very sparingly soluble, and which consist only of a Base combined with an Acid, or of a Metal combined with a Non-metallic body; the constituents of such compounds being among those above-mentioned 19

This First Part contains instructions for detecting the constituents of the chemical compounds of most frequent occurrence. The operations here described make known the chemical nature of the substances submitted to examination, but have no regard to their quantity. In the first three sections of this Part, the analyses have for object the detection of the constituents of compounds which consist only of a Base and an Acid, or of a Metal and a Non-metallic body. These analyses are especially intended for the use of beginners, who, for their own improvement, wish to exercise themselves in analytical examinations. It is proper that a student's experimental career should commence with substances having this simple constitution.—The three succeeding sections, on the contrary, contain full instructions for detecting the chemical constituents of either simple or mixed compounds. These sections teach the qualitative examination of inorganic substances, whose constituents are unknown, but are not such as very seldom occur. The instructions given in the latter sections suppose the operator to be acquainted with the analyses described in the first three sections.—The seventh section relates to the behaviour of the most important chemical substances towards reagents.

QUALITATIVE ANALYSIS.

SECTION I.

Instructions for the qualitative examination of compounds which are soluble in water, and which consist only of a Base combined with an Acid, or of a Metal combined with a Non-metallic body; the constituents of such compounds being among the substances in the following list.

BASES.

1. Potash.
2. Soda.
3. Ammonia.
4. Barytes.
5. Strontian.
6. Lime.
7. Magnesia.
8. Alumina.
9. Protoxide of Manganese.
10. Oxide of Zinc.
11. Oxide of Cobalt.
12. Oxide of Nickel.
13. Protoxide of Iron.
14. Peroxide of Iron.
15. Oxide of Cadmium.
16. Protoxide of Lead.
17. Oxide of Bismuth.
18. Deutoxide of Copper.
19. Oxide of Silver.
20. Protoxide of Mercury.
21. Peroxide of Mercury.
22. Oxide of Gold.
23. Protoxide of Tin.
24. Peroxide of Tin.
25. Protoxide of Antimony.

ACIDS AND NON-METALLIC BODIES.

1. Sulphuric Acid.
2. Nitric Acid.
3. Phosphoric Acid.
4. Arsenic Acid.
5. Boracic Acid.
6. Carbonic Acid;

or, the compound, instead of an acid, contains

7. Chlorine
8. Fluorine
9. Sulphur

} combined with a metal of the above-named bases.

I. *Course of the Analysis, to discover the Base or the Metal.*

A. The concentrated solution, in water, of the substance to be examined, is made somewhat acid. This is best effected by a few drops of muriatic acid, excepting oxide of silver, protoxide of mercury, or even a large quantity of protoxide of lead be present; in these cases, acetic acid or diluted nitric acid must be employed. The presence of the above oxides is known, when the addition of muriatic acid to the solution, produces a white precipitate. So much liquid sulphuretted hydrogen (which must be fully saturated with sulphuretted hydrogen gas) is next added, as is sufficient to cause the liquor to smell distinctly of sulphuretted hydrogen. If no precipitate is thereby produced, the base is one of those from No. 1 to No. 13; but if a precipitate appears, the base belongs to those from No. 14 to No. 25. Of course, then, it is either peroxide of iron, oxide of cadmium, protoxide of lead, oxide of bismuth, deutoxide of copper, oxide of silver, protoxide of mercury, peroxide of mercury, oxide of gold, protoxide of tin, peroxide of tin, or protoxide of antimony.

If the precipitate formed by the liquid sulphuretted hydrogen is black, then the base is one of those from No. 16 to No. 22. It is consequently either protoxide of lead, oxide of bismuth, deutoxide of copper, oxide of silver, protoxide of mercury, peroxide of mercury, or oxide of gold. These bases are discriminated by the following experiments:

To a small quantity of the dissolved compound, ammonia is added. If the solution acquires an intense blue colour, and no precipitate, insoluble in excess of ammonia, is formed, the base is deutoxide of copper.

A portion of the very concentrated solution of the compound is diluted with a large quantity of water. If a milkiness is occasioned, the base is oxide of bismuth.

To a portion of the solution, the operator adds a drop, or a few drops, of muriatic acid. If this produces a white precipitate, which remains insoluble when the solution is diluted with a large quantity of water, the base is either oxide of silver or protoxide of mercury. These two bases are distinguished by the following experiments:

To a portion of the solution of the compound, the operator adds one drop, or at most a few drops, of caustic ammonia. If this produces an intensely black precipitate, which redissolves in no excess of ammonia, but is merely rendered less black thereby; or if, when the solution is very acid, the addition of ammonia produces a grey precipitate, not soluble in an excess of ammonia, then the base is protoxide of mercury.

If, however, one drop, or at most a few drops, of caustic ammonia produce a brown precipitate, which, on the addition of a greater quantity of ammonia, immediately disappears, or if, when the solution is acid, no precipitate is produced by ammonia, then the base is oxide of silver.

To a portion of the solution, the operator adds a solution of caustic potash in excess. If a yellow precipitate is produced, the base is peroxide of mercury.

To a portion of the solution, a solution of protosulphate of iron is added. If a brown precipitate is formed, which, on its deposition, proves to be metallic gold, the base is oxide of gold.

The operator adds to the dissolved compound a little diluted sulphuric acid or the solution of a sulphate. If a white precipitate is produced, the base is protoxide of lead.

If the precipitate formed by the liquid sulphuretted hydrogen is milk-white, the base is peroxide of iron.

If the precipitate formed by the liquid sulphuretted hydrogen is yellow, the base is either peroxide of tin, or oxide of cadmium. These two bases are distinguished from each other by the following experiments:

Hydrosulphuret of ammonia is added to a portion of the solution. If the solution is acid, it must previously be neutralised by ammonia. The production of a yellow precipitate, not soluble in an excess of the precipitant, is an indication of oxide of cadmium.

If the addition of hydrosulphuret of ammonia to a portion of the solution previously neutralized by ammonia, produces a yellow precipitate which is easily dissolved by an excess of hydrosulphuret of ammonia, then the base is peroxide of tin.

If the precipitate produced by the liquid sulphuretted hydrogen is dark brown, the base is protoxide of tin.

If the precipitate produced by the liquid sulphuretted hydrogen is orange red, the base is protoxide of antimony.

B. If the acid solution of the substance under examination gives no precipitate with liquid sulphuretted hydrogen, the base is not one of those from No. 14 to No. 25. In this case, hydrosulphuret of ammonia is added to a neutral solution of the compound. (When the solution is acid, it must previously be neutralised by ammonia.) If a precipitate is thereby produced, the base is one of those from No. 8 to No. 13, and does not belong to those from No. 1 to No. 7. Consequently, it is either alumina, protoxide of manganese, oxide of zinc, oxide of cobalt, oxide of nickel, or protoxide of iron.

If the precipitate produced by the hydrosulphuret of ammonia is black, the base is one of those from No. 11 to No. 13. These three bases, oxide of cobalt, oxide of nickel, and protoxide of iron, are distinguished from one another by the following experiment:

To a portion of the solution, a solution of carbonate of potash or soda is added. If the precipitate thereby produced is first white, then green, and finally brownish red at the surface, the base is protoxide of iron.—If it is dirty red, the base is oxide of cobalt.—If it is bright green, the base is oxide of nickel.

If the precipitate formed by the hydrosulphuret of ammonia with the dissolved compound, is flesh red, the base is protoxide of manganese.

If, on the contrary, the precipitate is white, the base is either oxide of zinc or alumina. These two bases are distinguished from one another by the following experiments:

To a portion of the solution, caustic ammonia is added. If a white precipitate is produced, which disappears on the addition of an excess of ammonia, the base of the salt is oxide of zinc.

If the precipitate thereby produced, is insoluble in an excess of ammonia, the base is alumina.

C. If neither the acidulated solution of the substance under examination affords a precipitate with liquid sulphuretted hydrogen, nor the neutral solution with hydrosulphuret of ammonia, the base does not appertain to those from No. 8. to No. 25, but to those from No. 1 to No. 7. It is consequently potash, soda, ammonia, barytes, strontian, lime, or magnesia.—To a portion of the neutral solution of the compound a solution of carbonate of potash is added. If a white precipitate is produced, the base is one of those from No. 4. to No. 7, and does not belong to those from No. 1 to No. 3.

To distinguish from one another the four bases, from No. 4 to No. 7,—barytes, strontian, lime, and magnesia,—caustic ammonia is added to the neutral solution. The production of a white and flocculent precipitate indicates magnesia. It is necessary to observe here, that if the solution, instead of being neutral, is acid, ammonia produces no precipitate, even if magnesia be present.

To distinguish from one another the three bases which are not precipitated from the neutral solution by ammonia (barytes, strontian, and lime), hydrofluosilicic acid is added to the solution of the salt. If, after some time, a precipitate is formed, the base is barytes. If no precipitate appears, the base is lime or strontian.

To distinguish between these two bases, lime and strontian, a portion of the solution is diluted with a large quantity of water, and is tested with some drops of a solution of sulphate of potash, or a little very dilute sulphuric acid. If a precipitate is immediately produced, the base is strontian. If no immediate precipitate is produced, but if, after some time, there appears a crystalline precipitate, the base is lime.

D. If neither the acidulated solution of the substance under examination gives a precipitate with liquid sulphuretted hydrogen, nor the neutral solution with hydrosulphuret of ammonia or with carbonate of potash, the base does not appertain to those from No. 4 to No. 25, but to those from No. 1 to No. 3, and is consequently potash, soda, or ammonia.

To distinguish these three bases from one another, a concentrated solution of caustic potash is added to the concentrated solution of the compound. If an ammoniacal odour is produced, and if, when a glass rod moistened with muriatic acid is held over the surface of the liquid, white clouds are formed, the base is ammonia.

If this is not the case, an alcoholic solution of chloride of platinum is added to a portion of the concentrated solution of the salt. If this produces a yellow precipitate, the base is potash. If no precipitate is formed, the base is soda.

II. *Method of proceeding to discover the Acid, or the Non-metallic Body.*

A. To a portion of the dissolved compound, muriatic acid is added. If effervescence ensues, the acid is carbonic acid, or else the solution contains sulphur combined with a metal of one of the above-named twenty-five bases.

If the gas discharged during the effervescence possesses the well known odour of sulphuretted hydrogen gas, the solution contains a sulphuret. But if the gas is inodorous, the acid of the compound is carbonic acid.

B. If muriatic acid produces no effervescence, the operator adds a solution of chloride of barium to the neutral solution of the compound, the latter not being too much diluted with water. If a white precipitate is produced, the acid is either the sulphuric, phosphoric, arsenic, or boracic, or else the solution contains fluorine combined with a metal of one of the above-named twenty-five bases. These substances are distinguished from one another by the following experiments:

To the precipitate, produced by chloride of barium in the neutral solution, a little free acid is added; that which it is best to use, being muriatic acid. If the precipitate rests unaltered, the acid of the compound is sulphuric acid. If, on the contrary, the precipitate dissolves in the free acid, the acid of the compound is phosphoric, arsenic, or boracic acid, or else the solution contains fluorine combined with a metal of one of the above-named twenty-five bases. These compounds are distinguished from one another by the following experiments:

Concentrated sulphuric acid is poured over a portion of the dry compound in a platinum crucible, and a flat piece of glass covered with wax, through which some written characters have been traced, is laid thereon. The crucible is then gently warmed; and if, after cooling, the glass plate is found to be corroded where the characters were traced through the wax, the substance under examination is a fluoride.

If this is not the case, a portion of the pulverised compound, contained in a crucible of platinum or porcelain, or in a little porcelain capsule, is moistened with a drop, or a few drops, of sulphuric acid; some alcohol is then added, and is inflamed. If the mixture burns with a green flame, the acid of the compound is boracic acid.

If neither boracic acid nor fluorine is present, a portion of the solution of the compound is rendered somewhat acid, which is best done by the addition of muriatic acid. Thereupon, liquid sulphuretted hydrogen is added, and the whole is boiled.—If a yellow precipitate is formed, the acid of the compound is arsenic acid.

If this does not occur, and the operator has convinced himself, that neither boracic acid nor fluorine is present, then the acid of the compound is phosphoric acid.

C. When it has been found, by means of the above-described experiments, that the substance contains neither carbonic, sulphuric, boracic, arsenic, nor phosphoric acid, nor yet sulphur nor fluorine, the next experiment to be made, is to add to a portion of the solution, a solution of nitrate of silver. If this produces a white precipitate, not soluble in diluted nitric acid, then the compound contains chlorine in combination with a metal of one of the above-named twenty-five bases.

D. If it has been found, that neither carbonic, sulphuric, boracic, arsenic, nor phosphoric acid, nor yet sulphur, fluorine, nor chlorine, is present, a portion of the dry compound is strewn upon red-hot coals. If the combustion of the coals is thereby promoted in a very lively manner, and is accompanied by the noise of deflagration, the acid of the compound is nitric acid.

When, by following the methods here described, the base and the acid of the compound appear to have been determined, it is still necessary, that the analyst convince himself, by farther experiments, of the accuracy of the results he has obtained. I shall therefore describe in the seventh section of this part the manner in which the bases and acids behave with a variety of reagents, in order that the analyst may be able to submit the substance under examination to the most rigid tests.

SECTION II.

Instructions for the qualitative examination of compounds which are either quite insoluble, or very sparingly soluble, in water, which however are soluble in muriatic or nitric acid, and which consist only of a base combined with an acid, or of a metal combined with a non-metallic body; the constituents of such compounds being among those which are mentioned at page 5.

If the substance to be examined be very sparingly soluble, or quite insoluble in water, it must, if possible, be dissolved in an acid. For this purpose, muriatic acid is in most cases best adapted. The compound is mixed in a little glass vessel with the acid, which must be in a moderately diluted state. If the solution does not proceed quickly enough, the mixture is heated; whereupon, in most cases, a complete solution is effected. Whenever a salt occurs which has protoxide of mercury, oxide of silver, or protoxide of lead for base, it is necessary, instead of muriatic acid, to use nitric acid. When also the compound is a sulphuret, nitric acid must be employed, and the decomposition of the compound must be assisted by heat.

I. *Method of proceeding, to detect the Base or the Metal.*

The acid solution of the insoluble salt is diluted with water, and first treated with liquid sulphuretted hydrogen. If a precipitate is produced, the base of the salt belongs to those from No. 14 to No. 25, and is either peroxide of iron, oxide of cadmium, protoxide of lead, oxide of bismuth, deutoxide of copper, oxide of silver, protoxide of mercury, peroxide of mercury, oxide of gold, protoxide of tin, peroxide of tin, or protoxide of antimony. To distinguish these bases from one another, the process is to be followed which has been described from page 6 to page 8. Hereby it must be observed, that if arsenic acid be contained in the insoluble salt, the addition of sulphuretted hydrogen gas to the acid solution of the salt, produces also a precipitate of sulphuret of arsenic. In most cases, however, it is easy to throw down the precipitable metals from acid solutions by means of sulphuretted hydrogen gas, sooner than the arsenic acid. The latter is only precipitated by sulphuretted hydrogen gas after some time, and the precipitation can be quickened only by exposing the mixture to heat. On the other hand, the oxides are precipitated both sooner and with characteristic colours. These metallic sulphurets can be separated by a rapid filtration; and the filtered solution, which must smell strongly of sulphuretted hydrogen, can be boiled, in order that it may be ascertained, whether a precipitate of sulphuret of arsenic be still producible. To confirm what may be discovered by this experiment, the examination of the insoluble salt for arsenic acid, by means of the blowpipe, in the manner which will be described hereafter, must never be omitted.

If no precipitate is produced in the acid solution of the salt by liquid sulphuretted hydrogen, the base does not appertain to those from No. 14 to No. 25. In this case, the acid solution is supersaturated with ammonia, and hydrosulphuret of ammonia is added. If a black precipitate is thereby produced, or if by the mere supersaturation of the solution with ammonia a precipitate appear, which becomes black on the addition of hydrosulphuret of ammonia, then the base belongs to those from No. 11 to No. 13, and is either protoxide of iron, oxide of nickel, or oxide of cobalt. In order to determine which of these it is that the salt contains, a small quantity of the solid salt is examined before the blowpipe, by means of which the oxide of cobalt is particularly easy of detection. On the other hand, protoxide of iron and oxide of nickel are somewhat more difficult of discrimination. When no sure result respecting the identity of these two oxides has been obtained by using the blow-pipe, a little of the acid solution of the salt must be tested by a solution of prussiate of potash. (See Section VII.)

If the precipitate produced by hydrosulphuret of ammonia possess the peculiar flesh-red colour which characterises sulphuret of manganese, or if by the supersaturation of the acid solution with ammonia, a precipitate was formed which acquired this flesh-red colour on the addition of hydrosulphuret of ammonia, the base of the salt is protoxide of manganese.

If, on the contrary, the supersaturation of the acid solution of the salt by ammonia produced a white precipitate, of which the colour was not changed on the addition of hydrosulphuret of ammonia, the base is either oxide of zinc or alumina. There are four other substances, however, magnesia, lime, strontian, and barytes, which are also capable of being precipitated by ammonia, in the cases where they are combined, in insoluble salts, with phosphoric or boracic acid, or when their metallic bases are combined therein with fluorine. In order to distinguish these substances from one another, the following experiments must be made:—

The presence of oxide of zinc is detected, when a portion of the solid insoluble salt is mingled with soda, and heated on charcoal, in the inner flame of the blowpipe, or when it is merely moistened with solution of cobalt and exposed to the blowpipe flame. These operations are described in a succeeding section. Moreover, when the quantity of ammonia, employed to saturate the acid solution of the zinc salt, is considerable, the precipitate which it produces at first, redissolves, and forms a clear solution. Hydrosulphuret of ammonia, however, produces in this solution a white precipitate, which is insoluble both in caustic potash and ammonia.

The presence of alumina is detected, when a portion of the solid salt, moistened with solution of cobalt, is heated before the blowpipe. Moreover, the precipitate produced by the supersaturation of the acid solution by ammonia, is soluble in an excess of a solution of caustic potash. And even when hydrosulphuret of ammonia has been added, the precipitate produced by ammonia preserves its property of being soluble in caustic potash.

phuretted hydrogen gas to the acid solution of the salt, produces also a precipitate of sulphuret of arsenic. In most cases, however, it is easy to throw down the precipitable metals from acid solutions by means of sulphuretted hydrogen gas, sooner than the arsenic acid. The latter is only precipitated by sulphuretted hydrogen gas after some time, and the precipitation can be quickened only by exposing the mixture to heat. On the other hand, the oxides are precipitated both sooner and with characteristic colours. These metallic sulphurets can be separated by a rapid filtration; and the filtered solution, which must smell strongly of sulphuretted hydrogen, can be boiled, in order that it may be ascertained, whether a precipitate of sulphuret of arsenic be still producible. To confirm what may be discovered by this experiment, the examination of the insoluble salt for arsenic acid, by means of the blowpipe, in the manner which will be described hereafter, must never be omitted.

If no precipitate is produced in the acid solution of the salt by liquid sulphuretted hydrogen, the base does not appertain to those from No. 14 to No. 25. In this case, the acid solution is supersaturated with ammonia, and hydrosulphuret of ammonia is added. If a black precipitate is thereby produced, or if by the mere supersaturation of the solution with ammonia a precipitate appear, which becomes black on the addition of hydrosulphuret of ammonia, then the base belongs to those from No. 11 to No. 13, and is either protoxide of iron, oxide of nickel, or oxide of cobalt. In order to determine which of these it is that the salt contains, a small quantity of the solid salt is examined before the blowpipe, by means of which the oxide of cobalt is particularly easy of detection. On the other hand, protoxidè of iron and oxide of nickel are somewhat more difficult of discrimination. When no sure result respecting the identity of these two oxides has been obtained by using the blow-pipe, a little of the acid solution of the salt must be tested by a solution of prussiate of potash. (See Section VII.)

If the precipitate produced by hydrosulphuret of ammonia possess the peculiar flesh-red colour which characterises sulphuret of manganese, or if by the supersaturation of the acid solution with ammonia, a precipitate was formed which acquired this flesh-red colour on the addition of hydrosulphuret of ammonia, the base of the salt is protoxide of manganese.

If, on the contrary, the supersaturation of the acid solution of the salt by ammonia produced a white precipitate, of which the colour was not changed on the addition of hydrosulphuret of ammonia, the base is either oxide of zinc or alumina. There are four other substances, however, magnesia, lime, strontian, and barytes, which are also capable of being precipitated by ammonia, in the cases where they are combined, in insoluble salts, with phosphoric or boracic acid, or when their metallic bases are combined therein with fluorine. In order to distinguish these substances from one another, the following experiments must be made:—

The presence of oxide of zinc is detected, when a portion of the solid insoluble salt is mingled with soda, and heated on charcoal, in the inner flame of the blowpipe, or when it is merely moistened with solution of cobalt and exposed to the blowpipe flame. These operations are described in a succeeding section. Moreover, when the quantity of ammonia, employed to saturate the acid solution of the zinc salt, is considerable, the precipitate which it produces at first, redissolves, and forms a clear solution. Hydrosulphuret of ammonia, however, produces in this solution a white precipitate, which is insoluble both in caustic potash and ammonia.

The presence of alumina is detected, when a portion of the solid salt, moistened with solution of cobalt, is heated before the blowpipe. Moreover, the precipitate produced by the supersaturation of the acid solution by ammonia, is soluble in an excess of a solution of caustic potash. And even when hydrosulphuret of ammonia has been added, the precipitate produced by ammonia preserves its property of being soluble in caustic potash.

The presence of strontian and barytes is known by the production of a white precipitate, when diluted sulphuric acid is added to the acid solution of the salt, previously diluted with a large quantity of water. To distinguish these two bases from one another, hydrofluosilicic acid is added to the acid solution of the salt, previously diluted with water; whereupon, if barytes be present, a precipitate is produced after a short time; on the contrary, if strontian be present, no precipitation occurs.

The presence of lime is detected by adding to the concentrated acid solution of the salt, first sulphuric acid, and then alcohol. If a white precipitate appears, the presence of lime may be considered as certain, provided it has previously been ascertained, that neither barytes nor strontian is contained in the solution.

The presence of magnesia in the solid salts which are insoluble in water, can be best determined by means of the solution of cobalt, before the blowpipe. The operator is led almost to the certainty that magnesia is the base of the salt under examination, when he has found that none of the other earthy bases are contained in it.

If the acid solution of the salt gives no precipitate with sulphuretted hydrogen gas, nor yet when it is first supersaturated with ammonia, and then mingled with hydrosulphuret of ammonia, the next process is to add to a portion of the acid solution of the salt previously diluted with water, a solution of carbonate of potash. If, after the solution has been supersaturated with alcali, there appears a precipitate, either immediately, or when the mixture has been boiled for some time, then the base of the salt is one of those from No. 7 to No. 4; that is to say, it is magnesia, lime, strontian, or barytes.

To distinguish these from one another, the acid solution of the salt, previously very much diluted, is mingled with a little diluted sulphuric acid, or a solution of sulphate of potash. If a precipitate is immediately produced, the base is either strontian or barytes.—The presence of the latter earth is known, when hydrofluosilicic acid, on being added to another portion of the diluted acid solution, produces after some time, a white precipitate.

If barytes and strontian are not present, lime is detected by saturating the solution with ammonia, adding a solution of sal ammoniac, and then testing the mixture with the solution of an oxalate, which in such circumstances produces with lime a white precipitate.

But if no precipitate is produced by the oxalate, the same solution is tested with phosphate of soda. If there now appears a white precipitate, notwithstanding that the solution contains free ammonia, one may be convinced of the presence of magnesia.

The compounds which are insoluble in water are not examined for alcalies, because the acids which are here taken into consideration, produce with alcalies none but soluble compounds.

II. *Method of proceeding, to detect the Acid or the Non-metallic Body.*

A portion of the dry salt is first moistened with diluted muriatic acid. If an inodorous gas is disengaged with effervescence, it betokens carbonic acid. If the insoluble carbonate is not pulverised, but exposed to the acid, while in solid pieces, it often disengages the carbonic acid gas, only when the whole is warmed. It is best also, that the acid employed to decompose the carbonate, be not too concentrated. If the effervescence produced by diluted muriatic acid be accompanied by the discharge of a gas possessing the odour of sulphuretted hydrogen, it is a proof that the substance under examination, contains sulphur combined with a metal.

In the next place, the insoluble compound is tested for nitric acid by projection on glowing coals. This acid can only be present, when the compound is a salt with excess of base. It is also examined, before the blowpipe, on charcoal, for arsenic acid, whose presence, however, has already been detected by an experiment undertaken to find the base of the salt.

It is then tried, whether the compound, mixed and heated with sulphuric acid, in a platinum crucible, disengages a gas which corrodes glass. This effect indicates the presence of a fluoride. Or the compound is mingled with sulphuric acid and alcohol, and it is tried whether the latter burns with a green flame: if it does, the salt is a borate.

A portion of the compound is dissolved in nitric acid, if possible without heat, and the acid solution, diluted with water, is tested with a solution of nitrate of silver. If a white precipitate is produced, the substance under examination is a chloride.

A portion of the compound is heated in nitric acid. If a reaction takes place, accompanied by the disengagement of the yellow-coloured vapour of nitrous acid, and by the deposition of sulphur, which however does not occur at the begining of the operation, but only displays its characteristic colour after a prolonged digestion with nitric acid, and if farther, the acid solution, diluted with water, gives with a solution of nitrate of barytes, a white insoluble precipitate, it may be gathered from these phenomena, that the compound is a sulphuret. Nevertheless, if the compound be the sulphuret of mercury, nitric acid alone does not effect its decomposition, for which it is necessary to employ aqua regia; the gas which is disengaged, in this case, is not nitrous acid, but chlorine: however, the substance belongs then to those which will be taken into consideration in the third section. If the compound be the sulphuret of lead, of tin, or of antimony, there is produced by the digestion with nitric acid, a deposit, which consists not of sulphur alone but also of sulphate of lead, or peroxide of tin, or protoxide of antimony. In the two last cases also, the decomposition of the sulphuret must be effected by aqua regia, instead of by nitric acid.

Finally, the diluted solution of the salt in muriatic acid, is tested with a solution of chloride of barium, or the solution of the salt in nitric acid, is tested with a solution of nitrate of barytes. If a white insoluble precipitate be thereby produced, the acid of the salt is sulphuric acid. This, however, can never be the case, except when the substance under examination is a salt with excess of base.

If the preceding experiments have not been sufficient to detect the acid, the compound must contain phosphoric acid. The presence of this acid, especially in insoluble compounds, is more difficult of demonstration than that of all the other acids. On this account, it is always necessary to make a variety of experiments, before coming to a decision.—This subject will be treated of at length, under the head of Phosphoric Acid, in Section VI

SECTION III.

Instructions for the qualitative examination of compounds, which both in water and in acids, are either quite insoluble, or very sparingly soluble, and which consist only of a base combined with an acid, or of a metal combined with a non-metallic body; the constituents of such substances being among those which are quoted at page 5.

To these compounds, only the following can belong: sulphate of barytes, sulphate of strontian, sulphate of lime, sulphate of lead, chloride of silver, protochloride of mercury, sulphuret of mercury; and a great many acid phosphates, and some acid arseniates, after having been strongly ignited.

With respect to the latter substances, they can only be decomposed by being boiled with concentrated sulphuric acid. They then become soluble in water, except they have barytes, strontian, lime, or protoxide of lead for base. They are recognised by the examination of a portion, for arsenic and phosphoric acids, before the blowpipe. Arsenic acid is very easy of detection thereby. One is led to detect the presence of phosphoric acid, by exposing the compound to the blowpipe flame, after having moistened it with sulphuric acid; the presence of phosphoric acid is, in this case, betokened by the communication of a greenish colour to the flame.

With respect to the other compounds, they are all characterised by a white colour. To this rule, the sulphuret of mercury forms an exception. This substance has either a black or red colour, and is thereby already discriminated from the others. But that it may be known with greater certainty, it is treated with aqua regia. Sulphur is thereupon deposited, and the solution when diluted with water, gives, with the solution of a barytic salt, a precipitate which is insoluble in acids. By testing the solution still farther with reagents, it is easy to detect the presence of peroxide of mercury. It is still easier to demonstrate by experiments in the dry way, that the substance under examination is sulphuret of mercury. Mingled with soda, and heated in a little glass tube which is closed at one end, it gives globules of mercury. Heated thus, without soda, both the red and the black sulphuret of mercury sublime unaltered, but the sublimate in both cases is a red powder.

Of the other compounds, of which chloride of silver can also often present a greyish black, and if in the fused state, a yellowish colour, the three last, namely, protochloride of mercury, chloride of silver, and sulphate of lead, are distinguished from the three first, sulphate of barytes, sulphate of strontian, and sulphate of lime, by immediately assuming a black colour, when, after being grossly pounded, they are moistened with hydrosulphuret of ammonia. The individual compounds are discriminated as follows:

A small quantity of the substance to be examined, is gently heated over a spirit lamp, in a little glass tube closed at one end. If the substance totally sublimes, it is protochloride of mercury; if it fuses, it is chloride of silver; if it remains unaltered, it is sulphate of lead. To prove the correctness of the results thus obtained, the substance is thereupon examined before the blowpipe, for mercury, silver, or lead.

If the substance remains unaltered, when it is moistened with hydrosulphuret of ammonia, the base of the compound is lime, strontian, or barytes, and the acid is sulphuric acid. These salts are more difficult to be discriminated. The compound is pulverised and boiled in water; the solution is filtered, and divided into two portions. To one of these portions, a solution of chloride of barium is added; to the other, a solution of an oxalate. If a white precipitate is formed with both, and if that with chloride of barium is insoluble in acids, the substance is sulphate of lime.

If nothing is dissolved when the substance is boiled in water, a portion of it must be pulverised and boiled with a solution of carbonate of potash or of soda. It is filtered. The filtered solution is supersaturated with muriatic acid, diluted with water, and tested with a solution of chloride of barium. If an insoluble precipitate is produced, the compound is either sulphate of strontian or sulphate of barytes. To distinguish these from each other, the remainder of the mixture obtained by boiling the substance with the alcaline carbonate, is mingled with muriatic acid, and filtered. The solution is concentrated by evaporation, mixed with alcohol, and inflamed. If the alcohol burns with a red flame, the substance is sulphate of strontian; if not, it is sulphate of barytes.—The filtered muriatic acid solution can also be tested by hydrofluosilicic acid: if, after some time, a precipitate is thereby produced, it indicates the presence of barytes; if none is formed, the substance under examination is sulphate of strontian.

SECTION IV.

Instructions for the qualitative examination of mixed compounds, which are easily soluble in water, and the constituents of which are among those quoted at page 5 [*].

I. *Method of proceeding to detect the Bases.*

A. THE concentrated solution of the salt in water is rendered somewhat acid, which is best done by means of a few drops of muriatic acid. But if oxide of silver, protoxide of mercury, or even a great quantity of protoxide of lead be present (which is easily known, from the production of a white precipitate on the addition of muriatic acid), it is necessary to employ diluted nitric acid for this purpose. So much sulphuretted hydrogen is then added to this solution, that the mixture distinctly smells of it. If a precipitate is produced thereby, especially when the solution is warmed, the bases belong to those from No. 15 to No. 25, that is to say, the compound may contain oxide of cadmium, protoxide of lead, oxide of bismuth, deutoxide of copper, oxide of silver, protoxide of mercury, peroxide of mercury, oxide of gold, protoxide of tin, peroxide of tin, and protoxide of antimony. Besides these, peroxide of iron can also be present, because when that base exists in an acid solution, the addition of sulphuretted hydrogen gas occasions the precipitation of sulphur. If the precipitate formed by this reagent in an acid solution of the compound, be white and milky, it is a proof that of all the bases which can be detected thereby, peroxide of iron alone is present. It is, moreover, possible that arsenic acid may be contained in the compound, yet in that case the bases combined with it can only be alcalies, unless there be also much free acid present. If the acidulated solution of the compound, on being warmed with liquid sulphuretted hydrogen, gives a yellow precipitate, which dissolves in hydrosulphuret of ammonia, the presence of arsenic acid can be decided on with certainty; and under the same circumstances, one can, with equal certainty, decide on the absence of metallic oxides and earths, because the compounds formed by these substances with arsenic acid are not soluble in water.

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[*] This and the two following sections treat, not only of the analysis of mixed substances, but also of such compounds as are more simply constituted, and consist only of a base and an acid; it being, however, supposed to be unknown to the operator, that these substances have this simple constitution.

The precipitate is allowed to settle; the solution is poured off as completely as possible, and the precipitate is then mixed, first with a little ammonia, and then with an excess of hydrosulphuret of ammonia.—If the precipitate is then fully redissolved, the compound may contain oxide of gold, protoxide of tin, peroxide of tin, and protoxide of antimony.

The solution in hydrosulphuret of ammonia is diluted with water, and decomposed by diluted muriatic acid, of which so much is added as is sufficient to render the solution somewhat acid. The sulphurets which were in solution, now precipitate, and each exhibits its characteristic colour. But, as a portion of sulphur is at the same time set at liberty in consequence of the decomposition of the hydrosulphuret of ammonia, and as this sulphur mingles and precipitates with the metallic sulphurets, the colours of the latter are paler than they would be were they unaccompanied by free sulphur. If several metals, whose sulphurets are soluble in hydrosulphuret of ammonia, are present together, they can be discriminated in the following manner:

Oxide of gold is easily recognised from the production of a reddish purple colour when the solution of the substance to be examined, previously diluted with a large quantity of water, is mingled with a few drops of a solution of protochloride of tin, which has previously been rendered clear by the addition of free muriatic acid.—Oxide of gold is also detected by the precipitation of brown-coloured metallic gold, when the diluted solution of the unknown compound is tested with a solution of protosulphate of iron.

The presence of protoxide of tin is known, in many cases, by the formation of a milky solution when the compound is mixed with a great quantity of water; but it is particularly discovered, by the production of a reddish purple colour, when the solution of the compound, previously diluted with much water, is mingled with a diluted solution of gold.

Peroxide of tin and protoxide of antimony are more difficult of detection, when they are accompanied by other metals, whose sulphurets are soluble in hydrosulphuret of ammonia. Their presence can then be best detected by the behaviour of the precipitated sulphurets before the blowpipe. Protoxide of antimony is also discovered by the occurrence of a milkiness when the muriatic acid solution of the compound, which must not contain too much free acid, is diluted with a large quantity of water. But when only one of these two oxides is present, and it is not accompanied by any other metal whose sulphuret dissolves in hydrosulphuret of ammonia, it can be very easily distinguished by the peculiar colour of its precipitated sulphuret.

If the precipitate produced in the acid solution by liquid sulphuretted hydrogen gas does not completely dissolve in hydrosulphuret of ammonia, or if it is altogether insoluble therein, the compound under examination may contain oxide of cadmium, protoxide of lead, oxide of bismuth, deutoxide of copper, oxide of silver, protoxide of mercury, and peroxide of mercury. The operator ascertains whether the hydrosulphuret of ammonia dissolves any thing, by the following experiments: After the digestion of the precipitate with that reagent, the solution is diluted with water, separated by filtration from the insoluble remainder, and mixed with an excess of muriatic acid. If only a milkiness from the presence of free sulphur, and no precipitate of a metallic sulphuret is produced, the hydrosulphuret of ammonia has dissolved nothing. An easier method is, to place a few drops of the filtered solution upon platinum foil, to evaporate the liquor over a spirit lamp, and to heat the foil to redness: if nothing remains on the platinum foil, the reagent contains nothing in solution.

The precipitated sulphuret is filtered on the smallest possible filter, and washed clean. It is next treated with pure nitric acid. Generally speaking, it is unnecessary, in qualitative examinations, to separate the precipitate from the filter; they can be digested together in the nitric acid. With the assistance of heat, the sulphuret is decomposed by the nitric acid: the metal becomes oxidised and is dissolved, while the sulphur is set at liberty, remains undissolved, and after a prolonged digestion acquires a yellow colour. When this is perceived, the solution is filtered from the insoluble sulphur.

Hereto, the sulphuret of mercury forms an exception. Unless the nitric acid be too strong, it does not act upon this substance, which remains undissolved after the digestion, and is known by the characteristic black colour, which it exhibits in such cases. The operator examines this sulphuret before the blowpipe, and thereby very easily detects the presence of mercury, which may be contained in the compound either as peroxide or protoxide. To determine which of the two oxides the compound contains, the sulphuret produced by the preceding experiments, is heated in a little glass tube closed at one end: if it sublimes unaltered, the peroxide is present; but if the sublimed sulphuret of mercury appears mingled with globules of metallic mercury, the compound contains the protoxide of that metal.

The residual sulphur may also contain a portion of undissolved sulphate of lead, when the compound contains protoxide of lead, and sulphuret of lead is consequently among the metallic sulphurets. But the greater part of the protoxide of lead is dissolved by the nitric acid, when the digestion is not too long continued.

When the solution has been filtered from the precipitated sulphur, if the addition of an excess of ammonia communicates a blue colour to the liquid, it indicates the presence of deutoxide of copper.—If another portion of the solution is tested with muriatic acid, and produces a white precipitate, which does not redissolve on the addition of much water, but disappears immediately when ammonia is added, it proves that the compound contains oxide of silver.—To another portion of the diluted solution, a little diluted sulphuric acid is added; if this produces a white precipitate, protoxide of lead is in the compound.—Another portion of the solution is concentrated by evaporation, in order to separate the greater part of the nitric acid; after which, a large quantity of water is added: if a milkiness is thereby produced, the compound contains oxide of bismuth.—The presence of oxide of cadmium in the compound, is recognised by mingling the precipitated sulphuret with soda, and heating it on charcoal, in the inner flame of the blowpipe. It then produces a brown coating, which must not be confounded with that which is produced under similar circumstances, by compounds of lead or bismuth.

B. The liquid which is separated from the sulphurets that were precipitated from the acidulated solution of the compound, by sulphuretted hydrogen gas, is submitted to the same treatment as it would have been had sulphuretted hydrogen gas not produced a precipitate in the acidulated solution. In the first place, however, it is examined whether the liquid still contains any fixed bases. For this purpose, a few drops of it are evaporated on platinum foil, and the solid matter which is left is heated to redness. If no fixed remainder is exhibited, the liquid contains no more fixed bases. If, however, a remainder is exhibited on the foil, the examination of the liquid must be continued. The liquid is supersaturated with ammonia, and the ammoniacal solution is mingled with hydrosulphuret of ammonia. From the precipitate thereby produced, one can decide on the presence of peroxide of iron, protoxide of iron, oxide of nickel, oxide of cobalt, oxide of zinc, protoxide of manganese, or alumina.

The precipitate thus formed is filtered and washed with water which has been mingled with a few drops of hydrosulphuret of ammonia. Thereupon, the filter and the precipitate are digested in diluted muriatic acid, and the digestion is continued till the whole ceases to smell of sulphuretted hydrogen gas. The solution is then separated by filtration, and heated with a little nitric acid. When the precipitate is not fully decomposed and dissolved by muriatic acid, which is the case when sulphuret of nickel or sulphuret of cobalt is contained among the sulphurets precipitated by the hydrosulphuret of ammonia, it must be digested with nitric acid, or, after the addition of muriatic acid, a portion of nitric acid must also be added.

Ammonia is added in excess to the acid solution; the precipitate thereby formed is separated by filtration and washed. It can contain peroxide of iron and alumina. If it appears white, it consists merely of alumina: if it appears brown, both alumina and peroxide of iron may be present. To determine this with certainty, the precipitate and the filter are put into a little muriatic acid. When the precipitate is dissolved, the solution is filtered and mixed with a solution of caustic potash, which must be added in excess. Hereupon the peroxide of iron is precipitated, while the alumina remains dissolved. The solution is filtered and mingled with a solution of muriate of ammonia, which, if alumina be present, produces a white precipitate.

The iron thus obtained in the state of peroxide, can have existed in the compound which is under examination, either as peroxide or protoxide: to a solution of this compound, a solution of gold is added; if this precipitates metallic gold, in the form of a brown powder, it is a proof of the presence of protoxide of iron.

If the solution which has been filtered from the precipitate formed by caustic ammonia, possess a blue colour, it betokens the presence of oxide of nickel: if it has a feeble rose-red colour, it shows that the compound contains oxide of cobalt. The oxide of cobalt is moreover very easily recognised, even when it occurs in the smallest quantities, and also when it is mingled with many other oxides, by the property it possesses of communicating an intense blue colour to a glass of microcosmic salt or borax when heated therewith, either in the outer or inner flame of the blowpipe.

The ammoniacal liquor is mingled with a solution of caustic potash. If a bright apple-green precipitate is produced, oxide of nickel is contained in the compound. If the precipitate is otherwise coloured, and if, when exposed to the air, it becomes brown, it indicates the presence of protoxide of manganese. It is exceedingly easy to convince one's self of the presence of this base, by an experiment with the blowpipe.

The solution which has been filtered from the precipitate produced by caustic potash, is again precipitated by hydrosulphuret of ammonia. The precipitate is roasted a little on charcoal before the blowpipe, and can then be very easily examined, before the blowpipe, for oxide of cobalt, oxide of zinc, and protoxide of manganese.

C. When the acidulated solution of the compound was supersaturated with ammonia and precipitated by hydrosulphuret of ammonia, the subsequent filtration gave a solution which still remains to be examined. The first thing to be discovered is whether it still contains fixed bases: This is best learned by evaporating a few drops on platinum foil, and igniting the dry residue. If nothing remains on the platinum, it is useless to carry any farther the examination for fixed bases, because, in this case, no more are contained in the solution. But if there be any residue, the solution may still contain magnesia, lime, strontian, barytes, soda, and potash. The solution is supersaturated with muriatic acid, in order that the excess of hydrosulphuret of ammonia may be decomposed; the mixture is warmed, and the heat is continued until the solution no longer smells of sulphuretted hydrogen; it is then filtered, to separate it from the finely-divided sulphur produced by the operation. To the filtered solution, a solution of carbonate of ammonia is poured, until it is in excess; the mixture is warmed, to drive away the disengaged carbonic acid gas. The precipitate hereby produced may consist of lime, strontian, and barytes. It is dissolved in muriatic acid, and a portion of the solution is tested with a drop or a few drops of very dilute sulphuric acid, or still better with a little of a pretty dilute solution of sulphate of potash. If a precipitate is produced immediately, it is possible that all the three earths may be present; but if the precipitate is troubled only after some time, lime alone is present. In the first case, a portion of the diluted solution is mixed with an excess of diluted sulphuric acid; the mixture is warmed and the precipitate is filtered. The filtered solution is somewhat supersaturated with ammonia, and tested with a solution of oxalic acid or of an oxalate. If a precipitate is thereby obtained, at least after some time, the presence of lime is indicated; but if no precipitate appears, one may be assured that this earth is absent.—The precipitate produced by sulphuric acid, which contains barytes or strontian, or both together, and, indeed, lime also, when the presence thereof has been found in the filtered liquid, but not when the filtered liquid has been found free from lime,—this precipitate is examined for strontian before the blowpipe, which, according to BERZELIUS (*Anwendung des Löthrohrs*, page 246), is best done in the following manner:—A portion is heated on charcoal, in the inner flame, for a long time; the hepatic mass thereby produced is laid on platinum foil and dissolved in a few drops of muriatic acid; the solution is evaporated to dryness; the salt is scratched from the platinum foil, and laid on a small, long, wedge-shaped strip of paper, which is moistened with alcohol and set on fire. If, at the point of contact with the salt, the flame is coloured red, the precipitate formed by sulphuric acid consists either of sulphate of strontian alone, or of sulphate of strontian and sulphate of barytes together. But if the flame be not coloured red, there is no strontian present.—To determine with precision, whether or not the strontian is accompanied by barytes, it is necessary to proceed as follows: A portion of the muriatic acid solution of the alcaline earths, is tested with hydrofluosilicic acid. If this, after a short time, produces a precipitate, barytes is present; if no precipitate appears, barytes is absent.—When lime, strontian, and barytes have been precipitated by carbonate of ammonia, the solution filtered from the precipitate may still contain magnesia, soda, and potash. A small quantity is first evaporated and ignited on platinum foil, in order to ascertain whether any fixed substance remain. To distinguish the individual fixed alcalies and the magnesia, a portion of the solution is tested with a solution of phosphate of soda. If this reagent, after some time, produces a white precipitate, it indicates the presence of magnesia. If this be not the case, the remaining portion of the solution is evaporated to dryness, and the remainder is heated to redness in a little porcelain crucible, and kept at that temperature until all the ammoniacal salts are volatilized. The remainder is dissolved in a very small quantity of water, a little alcohol is added, and the solution is tested with an alcoholic solution of chloride of platinum. If a bright yellow precipitate appears, the compound contains potash. But if no precipitate is produced, soda must be present. Yet, before coming to this conclusion, the operator must have convinced himself that magnesia is absent, and that the solution filtered from the carbonated earths still contains some fixed constituent. If, however, the chloride of platinum has indicated the presence of potash, it is still to be determined, in that case, whether soda is present. This alcali can be very easily detected, however, even when the quantity of potash preponderates, by taking a portion of the calcined salt, before it is dissolved in water for the purpose of being tested with chloride of platinum, and exposing it on a platinum wire to the action of the point of the inner flame of the blowpipe: if the outer flame is thereupon coloured blue, potash alone is present; but if it is coloured strongly yellow, the compound contains either soda alone, or soda and potash together. Thus, by the chloride of platinum, the operator can easily determine whether potash be absent or present; by the colouring of the blowpipe flame, he can draw the same conclusions with respect to soda.—If, however, the solution filtered from the carbonated earths really contains magnesia, the farther examination of its contents is rendered more difficult. A portion of the filtered solution is evaporated to dryness, the dry residue is heated to redness, and then dissolved in water. To this solution, a solution of acetate of barytes is added in excess, whereupon the sulphuric acid is separated by the precipitation of sulphate of barytes. The solution is again filtered, and now contains the excess of acetate of barytes, acetate of magnesia, and the alcalies, if they are present, also in the state of acetates. The solution is evaporated to dryness, and the dry residue is heated to redness. The product is put into water: the barytes and magnesia, which exist now in combination with carbonic acid, remain undissolved. If the heat has been very strong, the magnesia is deprived of carbonic acid and is reduced to the caustic state, yet it is still insoluble. But the alcalies, if these be present, dissolve in the water, and give a solution of alcaline carbonates. It is now easy to be convinced of the presence and nature of the alcalies in the solution, by changing them into chlorides by means of muriatic acid.

On account of the method of this analysis, it is impossible to detect the presence of ammonia. This is discovered by heating the substance to be examined in a solution of caustic potash. An ammoniacal odour is produced, and if a glass rod moistened with muriatic acid is held over the solution, white vapours are formed.

II. *Method of proceeding, to detect the Acids.*

A portion of the concentrated solution of the compound is first tested with diluted muriatic acid, in order to ascertain whether carbonic acid or sulphur be present. If effervescence is produced, and if the gas that escapes is inodorous, it is at once determined that carbonic acid is present and that sulphur is absent; but if the gas that escapes possesses the well known odour of sulphuretted hydrogen gas, then the compound contains sulphur in the state of a metallic sulphuret. In this case, it may also contain carbonic acid, whose presence will be farther indicated by another operation of the analysis.

Another portion of the concentrated solution of the compound, which must be neutral, or at least not acid, is tested with a solution of chloride of barium. Instead of the solution of chloride of barium, it is necessary, when the compound contains protoxide of lead, oxide of silver, or protoxide of mercury, to employ a solution of nitrate of barytes. If a precipitate is thereupon produced, the compound can have for constituents sulphuric acid, phosphoric acid, arsenic acid, boracic acid, and fluorine. When also carbonic acid is present, a precipitate can be thereby produced, on the addition of a solution of chloride of barium. —Hereupon, diluted muriatic acid is added, or instead thereof, diluted nitric acid, when nitrate of barytes has been employed as the precipitant. If the precipitate formed by the barytic salt is then completely redissolved, the compound contains no sulphuric acid. If it dissolves with effervescence, and does not reappear when the acid solution, which, however, must not contain too much acid, but only as little as possible, is boiled, and saturated with ammonia, it is a proof that the precipitate formed by the barytic salt, originates entirely from carbonic acid, the presence of which has already been found by another experiment. If it dissolves in the acid with effervescence, but reappears when the solution is saturated with ammonia, then is carbonic acid present in company with one or more of the above-named acids. If this, however, is not the case, the compound may still contain phosphoric acid, arsenic acid, boracic acid, and fluorine. The presence of arsenic acid is detected by the treatment with liquid sulphuretted hydrogen. The presence of no metallic oxide can render indistinct the colour of the precipitate thence originating; for if this acid be present, alcalies alone can accompany it, because the compounds which it forms with earths and metallic oxides are insoluble in water, except they have an excess of acid. It is still easier to convince one's self of the presence of arsenic acid, by means of the blowpipe. The presence of boracic acid is found, when the compound is mingled with sulphuric acid and alcohol, and the latter is set on fire, whereupon a greenish coloured flame is produced. The presence of fluorine is detected by the disengagement of vapours which corrode glass, when the compound is treated with sulphuric acid. The presence of phosphoric acid is, however, much more difficult of detection. If the operator has convinced himself that arsenic acid, boracic acid, and fluorine are absent, then he can ascertain the presence of phosphoric acid, by testing the concentrated solution of the compound, with a solution of chloride of barium or chloride of calcium: a precipitate is produced, which disappears on the addition of muriatic acid or nitric acid, and reappears when the acid is saturated with ammonia. But if those acids, or only one or some of them are present, he must satisfy himself of the presence or absence of phosphoric acid by other methods.—If, for example, of all those acids, only arsenic acid be present, it must be separated by means of liquid sulphuretted hydrogen. So much of this reagent is added, that the solution, which must previously have been rendered acid, strongly smells thereof. The mixture is boiled a little, and the precipitated sulphuret of arsenic is separated by filtration. By the examination of the clear solution, when it has been previously neutralised, the operator can ascertain by means of a solution of chloride of barium or chloride of calcium, whether phosphoric acid be present or absent.—If merely fluorine be present, the compound is mixed with sulphuric acid, and heated in a little platinum crucible, so long as it gives out vapours. The residue is dissolved in water, a little muriatic acid is added, and then a solution of chloride of barium. The precipitated sulphate of barytes is separated by filtration, and the filtered solution is saturated with ammonia; thereupon, the presence of phosphoric acid will be indicated by a precipitate.—If, however, boracic acid is present, one can soon ascertain whether phosphoric acid is also present. This is the case, when the precipitate which is produced by solutions of chloride of barium or chloride of calcium, does not disappear on the addition of a large quantity of water, which it does when it results from the presence of boracic acid alone.

If, now, a solution of chloride of barium has produced in the concentrated solution of the compound a precipitate which does not disappear on the addition of diluted muriatic acid or nitric acid, or of which only a portion is thereby dissolved, it shows that the compound contains sulphuric acid. Whether, in addition to this, the compound also contains arsenic acid, phosphoric acid, boracic acid, or fluorine, is learned by continuing the examination of the solution, previously filtered from the precipitated sulphate of barytes, in the manner which has just been described.

The presence of a chloride is demonstrated, when a solution of the substance to be examined produces, with a solution of nitrate of silver, a white precipitate, which is not dissolved by diluted nitric acid.

Finally, the presence of nitric acid is detected by strewing a little of the compound on glowing coals, upon which, if nitric acid be present, deflagration ensues. Moreover, the methods of detecting this acid, which will be described in a subsequent section, can be employed in this case.

SECTION V.

Instructions for the qualitative examination of mixed Compounds, which are either quite insoluble in water, or only soluble in part, but which are completely soluble in muriatic or nitric acid, and the constituents of which are among the substances mentioned at page 5.

THE compound to be examined is first treated with water. If a portion of it is dissolved, the solution is to be examined according to the method which has been described in Section IV.—If the compound does not dissolve in water, it must be dissolved in muriatic acid, or, when protoxide of lead, oxide of silver, or protoxide of mercury are present, in nitric acid. The action is promoted by the application of heat, especially when sulphurets are present. The insoluble substance which remains, when a portion of the compound has been dissolved by water, is treated by an acid in the same manner.

I. *Method of proceeding, to detect the Bases.*

The method of proceeding in this analysis, in order to discover the bases in the acid solution, is very similar to that prescribed in the fourth section, for the examination of compounds which are soluble in water. But as it was unnecessary, in the preceding analysis, to pay any regard to earths and metallic oxides whenever phosphoric, arsenic, carbonic and boracic acids were present, or, on the other hand, to search for these acids when earths and metallic oxides were present, since the compounds which these substances form with one another are not soluble in water, and as it is here necessary to take those compounds into consideration, so the method of the analysis is unavoidably subjected to several modifications. These are so extended as to include a process for the detection of sulphur, which in the preceding analysis was, for the reasons just mentioned, quite neglected when the compound contained metallic oxides.

A. The acid solution is mingled with liquid sulphuretted hydrogen, and the resulting precipitate is afterwards treated with hydrosulphuret of ammonia, precisely in the manner which has been described in the preceding instructions, at page 22. If the compound contains arsenic acid, this likewise gives a precipitate with liquid sulphuretted hydrogen, and the precipitated sulphuret of arsenic is likewise dissolved by the hydrosulphuret of ammonia. If in this case peroxide of tin and protoxide of antimony are also present, it is often difficult to discriminate the three substances with certainty, and to demonstrate their co-existence in the compound. The presence of arsenic acid is then easily detected, when the substance is treated with soda on charcoal before the blowpipe. The presence of protoxide of antimony is made known by the orange yellow precipitate which is formed, when the solution of the sulphuret in hydrosulphuret of ammonia is diluted with water, and decomposed by muriatic acid. But it is more difficult, when both these substances are present, to determine whether peroxide of tin be present or not. The best method of proceeding, in that case, is as follows: The solution of the sulphuret in hydrosulphuret of ammonia, is diluted with water and precipitated by diluted muriatic acid. The precipitated sulphuret is dried, and strongly heated in a glass tube closed at one end. When it is possible, the access of atmospheric air should be prevented during the ignition. By this operation, sulphur and sulphuret of arsenic are sublimed, and sulphuret of tin and sulphuret of antimony in minimum of sulphur remain behind. This remainder is dissolved, with the assistance of heat, in concentrated muriatic acid, and the solution is diluted with water. It then contains protoxide of antimony, accompanied by protoxide of tin, if the compound contained peroxide of tin. The presence of protoxide of tin in the solution, can be easily detected by means of a solution of gold.

If the sulphurets precipitated from the acid solution of the compound, by liquid sulphuretted hydrogen, have only partially or not at all dissolved in hydrosulphuret of ammonia, the compound may contain oxide of cadmium, protoxide of lead, oxide of bismuth, deutoxide of copper, oxide of silver, protoxide of mercury, and peroxide of mercury. These metals are discriminated by experiments performed according to the method described in the preceding section, at page 24.

B. The solution, separated from the precipitate produced by liquid sulphuretted hydrogen, is now examined, in the manner described in the preceding section, to ascertain whether it still contains any fixed bases. If this be the case, the solution is supersaturated with ammonia, and tested with hydrosulphuret of ammonia. The precipitate thereby produced can be attributed to the presence of peroxide of iron, protoxide of iron, oxide of nickel, oxide of cobalt, oxide of zinc, protoxide of manganese, and alumina. It may also contain magnesia, lime, strontian, and barytes, when the compound contains either these earths combined with phosphoric or boracic acids, or their metallic bases combined with fluorine. This precipitate is treated very nearly in the manner that, in the foregoing section, has been recommended for the examination of the bases precipitated under similar circumstances. It is digested with muriatic acid or aqua regia, and the filtered solution is in the first place heated with nitric acid. Thereupon, diluted sulphuric acid is added to the solution. If strontian and barytes are present, they are hereby fully precipitated, in the state of sulphate of strontian and sulphate of barytes. Lime also, if present in large quantity, and the solution is not too dilute, is partially precipitated. The liquid is filtered and the precipitate is treated with a large quantity of water: if none of it is dissolved, it can contain only sulphate of strontian and sulphate of barytes; but if a portion is dissolved, the strontian and barytes can be accompanied by lime. It is then easy to demonstrate the existence of lime in the filtered liquid, by testing it with the solution of an oxalate. The insoluble remainder, which may consist of sulphate of strontian and sulphate of barytes, is examined before the blowpipe, in the manner which has been described at page 28, in the preceding section. If this examination proves that strontian is absent, the insoluble sulphate contains merely barytes;

but if the experiment shows that strontian is present, the sulphate may still contain barytes also. In order to determine this with accuracy, the precipitated sulphates must be boiled with a solution of carbonate of potash, or carbonate of soda: the solution must be poured off, and the remainder treated with muriatic acid. In the solution formed by the muriatic acid, the presence of barytes can be detected by hydrofluosilicic acid.

The solution filtered from the earthy sulphates, is supersaturated with ammonia. By this means peroxide of iron and alumina are precipitated; but if the solution contain phosphoric acid, then magnesia also may be thrown down by the ammonia. The precipitate is boiled with a solution of caustic potash, wherein the alumina dissolves, while the peroxide of iron and the magnesia remain undissolved, the latter losing, by the operation, the greater part of its phosphoric acid. The alumina can be precipitated anew, by means of a solution of sal ammoniac. The presence of peroxide of iron, in the insoluble residue, is easily recognised by means of the blowpipe; but that of magnesia, it is more difficult to detect. The insoluble residue must be dissolved in muriatic acid, and the acid solution must be supersaturated with ammonia. Hereupon, the peroxide of iron precipitates, while the greater part of the magnesia remains in solution, and can be indicated by various reagents.

The solution which has been filtered from the precipitated peroxide of iron, alumina, and magnesia, can still contain the greater proportion of the oxide of nickel, oxide of cobalt, protoxide of manganese, and oxide of zinc. It must be examined precisely according to the method which has been described in the preceding section, at page 27.

C. The solution which had been supersaturated with ammonia, and then precipitated by hydrosulphuret of ammonia, having been filtered from the precipitate, remains still to be examined. In the first place, it must be found whether it still contain any fixed constituents. If this be the case, the farther analysis is carried on precisely according to the method described at letter *C*, in the preceding section (page 27).—It yet remains to be remarked, that it is scarcely necessary to apply reagents for the detection of the alcalies; because the acids which are here taken into consideration form only soluble salts with the alcalies.

II. *Method of proceeding, to detect the Acids.*

The discovery of the acids is more difficult with these compounds, than with those which are soluble in water.

The presence of carbonic acid is always, and that of sulphur sometimes, discovered, by the effervescence produced when the substances for examination are put into diluted muriatic acid. If the gas which escapes during the effervescence is inodorous, it is carbonic acid gas alone; but if the gas smells of sulphuretted hydrogen, the compound may contain both sulphur and carbonic acid. In this case, it is necessary to analyse the disengaged gas. With this view, a portion of the substance for examination is decomposed by diluted muriatic acid, in a glass which can be closed by a cork through which passes a little glass tube bent twice at a right angle. By means of this apparatus, the gas is led into a solution of chloride of barium, to which a little ammonia has previously been added. If the current of gas produces a white precipitate, which dissolves with effervescence in muriatic acid, the compound contains carbonic acid. It is necessary, in this experiment, to protect the solution of chloride of barium from the access of atmospheric air.

A portion of the compound is dissolved in muriatic acid, or, if oxide of silver, protoxide of mercury, or protoxide of lead, are present, in nitric acid. The solution is diluted with water, and tested with a solution of chloride of barium, or, if nitric acid instead of muriatic acid has been employed as a solvent, with a solution of nitrate of barytes. If, thereupon, a white precipitate appears, the compound contains sulphuric acid.—A portion of the compound is heated with nitric acid. If the decomposition is accompanied by the disengagement of yellow vapours of nitrous acid, and by the deposition of sulphur, and if the acid solution, filtered and diluted with water, produces with a solution of nitrate of barytes, a white precipitate, the compound contains a sulphuret. When the sulphur is combined with mercury, aqua regia instead of nitric acid must be employed to decompose it. In this case, chlorine is disengaged, and not nitrous acid. (See Section II. page 18.)

A portion of the compound is dissolved in nitric acid, if possible, without the aid of heat: the solution is diluted with water, and tested with a solution of nitrate of silver. The production of a white curdy precipitate, indicates the existence of a chloride in the compound.

It is next examined, whether the compound, on being mingled in a platinum crucible with sulphuric acid, disengages a gas capable of corroding glass. If it does, the presence of a fluoride is known.—It is mingled with sulphuric acid and alcohol, and the latter is inflamed, in order that it may be seen whether boracic acid be present, which is known by the green colour it communicates to the flame of burning alcohol.

The presence of nitric acid is detected by throwing a portion of the compound on burning coals.—The presence of arsenic acid is found by means of the blowpipe.

The presence of phosphoric acid is very difficult of detection in these compounds. The substance can be examined before the blowpipe, according to the process of BERZELIUS; yet it is necessary previously to ascertain the absence of arsenic acid, of sulphuric acid, and of sulphur, and also, according to the statement of FUCHS, of boracic acid.—The detection of phosphoric acid, in the wet way, is attended by many difficulties. If the bases contained in the substance to be examined consist solely of metals which can be precipitated from their acid solution by liquid sulphuretted hydrogen, the separation of the bases is effected by means of this reagent, the solution is filtered from the precipitated sulphurets, and is examined for phosphoric acid, in the manner which has been described in Section IV. (page 32). The solution must previously, however, be freed by heat from the excess of sulphuretted hydrogen. If phosphoric acid be precipitated by a solution of chloride of calcium or chloride of barium, from a solution previously rendered ammoniacal, it is still indispensably necessary to prove that the precipitate so formed is actually phosphate of lime or of barytes. With this object, it is examined for boracic acid and fluorine, and then tried before the blowpipe for phosphoric acid.—If, on the contrary, the bases consist of metallic oxides which can be precipitated by hydrosulphuret of ammonia from the acid solution previously supersaturated with ammonia, and are consequently comprised among peroxide of iron, protoxide of iron, oxide of nickel, oxide of cobalt, oxide of zinc, and protoxide of manganese, then they are submitted to the action of this reagent; the solution is filtered from the precipitate, mingled with diluted muriatic acid, and digested until it no longer smells of sulphuretted hydrogen. It is then separated from free sulphur by filtration, and examined for phosphoric acid after the same method.—If the bases consist of alumina, magnesia, lime, strontian, and barytes, the detection of phosphoric acid is difficult, especially if the compound contains also metallic oxides which can be precipitated only by hydrosulphuret of ammonia. If, on the other hand, these earths are alone, or are accompanied by such metallic oxides only, as can be precipitated from their acid solutions by liquid sulphuretted hydrogen, the presence of phosphoric acid can be detected in the following manner: The acid solution is precipitated by liquid sulphuretted hydrogen, filtered from the sulphurets, and supersaturated with ammonia. The earths are hereby precipitated, provided they were combined with phosphoric acid. Supposing now, that merely lime, strontian, and barytes, were present, the production of a precipitate by ammonia is a proof of the presence of phosphoric acid; nevertheless, the operator must convince himself that the precipitate contains neither fluorine nor boracic acid, and prove by the blowpipe, that it contains phosphoric acid. If the solution contain magnesia, that earth is also precipitated by ammonia, provided that phosphoric acid be present. This is the case even when the solution contains so much muriate of ammonia, that, were phosphoric acid absent, magnesia could not be precipitated by ammonia. Alumina is also precipitated; but the precipitation of this earth by ammonia, is no proof of the presence of phosphoric acid. The precipitated alumina must be examined for the phosphoric acid it may contain, in the manner which will be described under the head of Phosphoric Acid, in the seventh section.—But if the substance for examination contains not only these earths, but also peroxide of iron, protoxide of iron, oxide of nickel, oxide of cobalt, oxide of zinc, or protoxide of manganese, together with the metallic oxides which can be precipitated from acid solutions by liquid sulphuretted hydrogen, the examination must then be executed in quite another manner. The substance to be examined is dissolved in muriatic acid, and the solution is mingled with liquid sulphuretted hydrogen, in order that the metals precipitable by that reagent may be separated. The solution is filtered and heated until it ceases to smell of sulphuretted hydrogen. Thereupon, diluted sulphuric acid is added, by which barytes and strontian are precipitated, as also can lime be, provided a sufficient quantity of alcohol be added to the solution to render the sulphate of lime insoluble. The solution is filtered from the precipitate, and when lime has been precipitated, the solution is heated until all the alcohol has volatilized. If, now, the solution contains neither magnesia nor alumina, but only such metallic oxides as can be precipitated by hydrosulphuret of ammonia, the solution is rendered ammoniacal, the metals are precipitated by hydrosulphuret of ammonia, and the filtered liquid is examined for phosphoric acid in the manner already described. But if those two earths are present, the solution is mingled with an excess of a solution of caustic potash, and the mixture is boiled, whereupon, protoxide of iron, oxide of nickel, oxide of cobalt, protoxide of manganese and magnesia, precipitate. In most cases, a small proportion of the phosphoric acid is carried down by this precipitate, yet the principal part of it remains in the filtered solution, and can be therein detected in the following manner: A slight excess of muriatic acid is first added, and then a solution of chloride of barium, which produces a precipitate of sulphate of barytes. The solution is filtered, and mingled with ammonia, which precipitates phosphate of barytes.—But if oxide of zinc and alumina are present, the phosphoric acid dissolves with them in the caustic potash. If oxide of zinc alone is present, it is precipitated from the solution in caustic potash by hydrosulphuret of ammonia, and the presence of phosphoric acid is sought for in the filtered solution. If alumina alone is contained in the alcaline solution, the presence of phosphoric acid is then detected in the manner which will be described under the head of Phosphoric Acid, in the seventh section. But if both are present together, then hydrosulphuret of ammonia is added to the solution in caustic potash. Hereby the zinc alone is precipitated, in the state of sulphuret of zinc, while the alumina remains in solution with the phosphoric acid, provided a sufficient quantity of caustic potash be present. When the solution has been filtered from the sulphuret of zinc, and the excess of hydrosulphuret of ammonia has been decomposed, the presence of phosphoric acid and alumina can be detected in the filtered solution.

SECTION VI.

Instructions for the qualitative examination of mixed compounds, which are either totally insoluble, or of which the greater part is insoluble, both in water and diluted muriatic or nitric acid; the constituents of such substances being among those quoted at page 5.

If the compound for analysis has first been treated with water, and afterwards with a diluted acid, and still leaves an insoluble remainder, this remainder can consist only of the substances which have been taken into consideration in the third section, at page 19. These substances are the following: sulphate of barytes, sulphate of strontian, sulphate of lime, sulphate of lead, chloride of silver, protochloride of mercury, and sulphuret of mercury.

The presence of the protochloride of mercury, and also of the sulphuret of mercury is detected, when a portion of the insoluble remainder, after it has been dried, is strongly heated in a glass tube closed at one end. Both substances are thereby sublimed, and both without alteration, if they are contained alone in the residue; but if they are accompanied by a portion of any other free base, or by a metal, the sublimate exhibits little globules of mercury. When both substances volatilize undecomposed, they are in consequence easily recognised. The protochloride of mercury becomes black when it is put into ammonia. The sulphuret of mercury, upon being sublimed, produces a red powder.

The portion of the insoluble substance which does not volatilize when thus heated, may still contain chloride of silver, sulphate of lead, sulphate of lime, sulphate of strontian, and sulphate of barytes. This remainder is fused with about twice or thrice its weight of dry carbonate of soda. If it is known that no chloride of silver is present, the fusion may be effected in a platinum crucible; yet even then, the operation must be managed with caution, and the platinum crucible exposed merely to a low red heat, especially when sulphate of lead is present. In general, one can just as well make use of a little porcelain crucible, and when very great quantities are not employed, effect the fusion over a spirit lamp with circular wick. When the melted mass has become cool, it is treated with water, and allowed to soften: more water is then added, the whole is digested, and the liquid is filtered from the insoluble remainder, and supersaturated with nitric acid. A solution of nitrate of barytes, on being added to this acid solution, indicates the presence of sulphuric acid; a solution of nitrate of silver, added to another portion, indicates the presence of chloride of sodium, when chloride of silver has formed part of the compound. The undissolved portion can now consist of carbonates of barytes, strontian, lime, and lead. It can also contain metallic silver, if chloride of silver has been present in the compound. When a very strong heat has been employed in the fusion, the silver is found as a metallic bead at the bottom of the crucible: when the heat has been less strong, so that the whole could not fully melt, the silver is obtained in a finely-divided state, upon treating the mass with water. The remainder is dissolved in nitric acid; yet, if silver and carbonate of lead are absent, it is better to employ muriatic acid as the solvent. A small portion of the solution is tested with diluted muriatic acid for oxide of silver: if this is present, there is a precipitate of chloride of silver. This is filtered, and the clear solution is mixed with caustic ammonia: if this produces a white precipitate, it shows the presence of protoxide of lead. If oxide of silver and protoxide of lead are contained in the compound, the greater part of the solution is treated with liquid sulphuretted hydrogen, in order to separate these two bases. The solution, filtered from the precipitate, and now possibly containing lime, strontian, and barytes, is tested with hydrofluosilicic acid. If this reagent, after some time, produces a precipitate, it indicates the presence of barytes. The solution is thereupon separated from the precipitate. If it now gives an immediate precipitate with a solution of sulphate of potash, or with very dilute sulphuric acid, it contains strontian, either alone or accompanied by lime. To determine the presence of the latter, the solution is filtered from the precipitated sulphate of strontian, when there is any, and is saturated with ammonia: if it then gives a white precipitate on being tested with the solution of an oxalate, it still contains lime.—The operator can also employ in the discrimination of these three earths, the method which has been described at page 28.

Many acid phosphates, some acid arseniates, and a few other compounds, are insoluble both in water and in acids when they have been exposed to a strong red heat. The presence of arsenic acid, and even that of phosphoric acid as well as of a variety of metallic oxides, can in this case be discovered by means of the blowpipe. If the operator has thus detected the presence of arsenic acid or of phosphoric acid, the pulverised substance must be digested in a platinum capsule with concentrated sulphuric acid, with which it must even be boiled for some time. The substance is thereby decomposed, and upon the addition of water, is dissolved. A solution is not obtained, however, when the base is of such a nature as to form with sulphuric acid a compound which is either insoluble or but very sparingly soluble. The bases which cannot be dissolved by this treatment, are protoxide of lead, lime, strontian, and barytes; these four bases are analysed according to the instructions which have been given above. —The solution is examined according to the method which has been described in the fifth section.

SECTION VII.

On the behaviour of Simple Substances and their most important Compounds, towards Reagents.

When the chemist desires to occupy himself with qualitative chemical inquiries, it is necessary for him to become acquainted with the action of reagents on the substances which commonly form the subjects of analysis. The preceding sections of this part contain full instructions for detecting the constituents of various compounds, both of simple and complex constitution. In all cases of analysis, however, when the operator imagines that he has discovered the true constituents of a compound, it is necessary to treat the compound with such a variety of reagents as are sufficient to verify the accuracy of his results.

This section contains a description of the behaviour of the most important simple substances, and of their principal compounds, particularly those resulting from their combination with oxygen, towards the reagents which are most worthy of employment. Amongst these reagents, the greatest attention is paid to those with which each substance produces the most characteristic phenomena, and by which it is consequently most strikingly distinguished from other substances.

In order that the instructions given in the preceding sections might not be rendered too difficult, I considered it prudential to omit the consideration of certain substances, notwithstanding that some of them are of frequent occurrence in analysis. In the present section, however, I shall describe how it is that these substances are detected in qualitative examinations.

As the presence of organic matter has frequently the effect of altering the action of reagents on inorganic bodies, I have considered it expedient to describe the processes, by the adoption of which the operator is led to obtain accurate results, under the circumstances alluded to.

A. BASES.

I. POTASH.

When pure, it is of a white colour; and very easily soluble in water, under disengagement of heat. The solution, even in a diluted state, has a very caustic taste, dissolves the skin of the tongue, and colours reddened litmus paper strongly blue. It deliquesces in the air, attracts carbonic acid from the atmosphere, and is gradually converted, first into carbonate, and finally into bicarbonate of potash. A solution containing potash in this altered state, effervesces on being supersaturated with an acid, because carbonic acid gas is then disengaged. When potash is heated in a vessel of silver, it fuses before it becomes red-hot. It dissolves in spirits of wine when free from carbonic acid.

The presence of potash, in solution in water, is indicated by the following substances.

A concentrated solution of *Tartaric Acid* added in excess to a concentrated solution of potash, immediately produces a crystalline precipitate of bitartrate of potash. When the solution of potash is dilute, the precipitate appears only after some time. The more slowly it is formed, however, the more distinctly is it crystallised. By an excess of any strong acid, as, for example, muriatic, nitric or sulphuric acid, or even by a solution of oxalic acid, the precipitate is dissolved; but it is neither dissolved by tartaric nor by acetic acid. Solutions of carbonated and caustic potash, soda, and ammonia dissolve the precipitate with ease; but the addition of a small quantity of a strong acid reproduces the precipitate, which may be again dissolved by a greater quantity of the same acid.

A spirituous solution of *Chloride of Platinum* produces in the solution of potash, a bright yellow precipitate of chloride of potassium and platinum. When the operator has but a small quantity of potash, it is best to dissolve it in spirits of wine, and then to add the spirituous solution of chloride of platinum. The resulting precipitate is not sensibly dissolved by free acid.

Hydrofluosilicic Acid produces in the solution of potash a precipitate of so transparent and gelatinous a condition, as to be scarcely perceptible. This is particularly the case, when the solution of potash is not very concentrated. The gelatinous precipitate very gradually subsides; but even after its deposition, it is only distinguishable by being less transparent than the supernatant solution, and by causing a play of colours. Upon being dried, it forms a white powder.—If the solution of potash be very concentrated, then the addition of hydrofluosilicic acid produces a white troubling, and the transparent gelatinous precipitate soon begins to subside; but in that case, there is no play of colours, such as there is with the precipitate which is deposited by very dilute solutions.—Free muriatic acid does not dissolve the precipitate; but it deprives it of its transparency, and renders it opalescent.

A solution of *Carbazotic Acid* in alcohol, produces, even in diluted solutions of potash, a bright yellow crystalline precipitate. It is best to employ an alcoholic solution of potash, when it is desirable to obtain a precipitate from a very small quantity. This reagent, which LIEBIG has recommended for the detection of potash, is still more sensible than the solution of chloride of platinum. When a solution of potash is so much diluted, that chloride of platinum no longer produces a precipitate, the alcoholic solution of carbazotic acid is still able to effect precipitation, if not immediately, yet after some time.

A concentrated solution of *Sulphate of Alumina* on being added to a concentrated solution of potash, after the latter has been saturated by an acid (for which purpose muriatic acid is best adapted), produces crystals of alum. These can generally be recognised as regular octahedrons with blunted angles. The crystals of alum do not effloresce in the air.

Before the *Blowpipe*, potash is detected, according to HARKORT, by fusing pure oxide of nickel with borax to a glass, and adding thereto the substance containing potash, by which the glass is coloured bluish. (BERZELIUS, *Anwendung des Löthrohrs*, p. 69).—According to FUCHS, the presence of potash can be much better detected as follows: A portion of the salt is fused on the platinum wire, and the flame of the blowpipe is so directed thereon, that the point of the interior flame touches the fused lead. The exterior flame is then distinctly violet coloured.

The salts of potash which are soluble in water, produce solutions which behave towards the above reagents, in a similar manner to the solutions of pure potash. *Tartaric Acid* produces in the concentrated solutions of potash salts, when added in excess, the same precipitate as in the solution of pure potash. In the solutions of such potash salts as are rather sparingly soluble, such as sulphate of potash, the precipitate does not appear till after some time.—The spirituous solution of *Chloride of Platinum* produces in the concentrated solutions of potash salts, the same bright yellow precipitate of chloride of potassium and platinum, that it produces in the solutions of pure potash. If the salt which is to be tested for potash be soluble in spirits of wine, it is best to mix a spirituous solution of the salt with the spirituous solution of chloride of platinum.—*Hydrofluosilicic Acid* behaves towards solutions of potash salts in the same manner as towards solutions of pure potash.—To detect the presence of potash in a very small quantity of a potash salt, by *Carbazotic Acid*, it is proper to employ a spirituous solution of the salt, provided it be soluble in spirits.—A concentrated solution of *Sulphate of Alumina*, added to concentrated solutions of several potash salts, produces, after some time, crystals of alum. This is particularly the case with concentrated solutions of sulphate and nitrate of potash, and of chloride of potassium. The neutral compounds of potash, with phosphoric, arsenic, and boracic acids produce with a solution of sulphate of alumina, a voluminous precipitate which contains alumina in combination with the acid of the particular potash salt employed in the precipitation. If in these cases the solutions be acid, they will often produce crystals of alum with the solution of sulphate of alumina. The production of alum crystals does not occur, however, till after a very long time. Their production can be hastened by adding sulphuric acid to the solution. Carbonate of potash and sulphuret of potassium must be converted by muriatic acid into chloride of potassium, when it is intended to form crystals of alum by subjecting them to the action of sulphate of alumina.—Before the *Blowpipe*, potash in the potash salts, is detected in the same manner as pure potash. A bead of borax in which pure oxide of nickel has been dissolved, is coloured blue by potash salts. But most potash salts are better detected by the violet colour communicated to the outer flame of the blowpipe, when a portion of the salt is fused on a platinum wire, and the bead is exposed to the point of the inner flame. This colouring of the flame is best produced by chloride, bromide, and iodide of potassium. It is more clearly exhibited by these than by pure potash. It is less distinctly exhibited by sulphate and carbonate of potash, and not at all by phosphate and borate of potash.

The neutral soluble salts of potash are for the most part capable of being heated to redness without suffering decomposition; indeed, they are very nearly all so, except nitrate of potash, provided that atmospheric air be excluded *.—The solutions of the neutral salts have partly no action on litmus paper, and partly turn reddened litmus paper blue. Sulphate and nitrate of potash, and chloride, bromide, and iodide of potassium, do not when dissolved in water affect the colour of litmus paper: but the neutral phosphate, arseniate, borate, and carbonate of potash, and the fluoride and sulphuret of potassium turn reddened litmus paper blue.

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* An instrument often spoken of in the following pages is the *spirit lamp with circular wick*, or with *double current of air*. I have given a figure of this lamp on the title-page of the work, and I shall now give a description of it. For both the figure and the description, I am indebted to a work recently published by MITSCHERLICH. The spirit lamp with circular wick is one of the most indispensable instruments of the analytical chemist. A great number of very accurate experiments cannot be performed without it.—The wick passes between two cylinders which are connected below by a horizontal plate, and are raised or

Potash produces very few salts which are insoluble or very sparingly soluble in water. In these salts, however, the presence of potash is often difficult of detection. In general, it can only be determined with certainty, after the acid has been separated from the potash. These compounds occur but seldom. They are formed only by weak acids, or by such acids as, in a pure state, are either inso-

depressed by means of the toothed wheel *e* and the toothed bar *g*. The lower end of the latter is connected with a cross bar, upon the end of which is fastened a ring whereon the wick is stuck. The cross bar works up and down in the box *b*. This box does not form part of the spirit-holder *a*, as it does in the common lamps; but is separated from it by the open spaces *t t*. The spirit passes, from *a* into *b*, by a small pipe which passes diagonally from the under part of *a* nearly to the bottom of *b*, something in this manner: V. The object of this contrivance is to prevent the explosion which frequently takes place when the common spirit lamps are inflamed, and which is owing to the mixture of atmospheric air and vapour of alcohol which exists in the spirit-holder *a*. At *m* is an opening by which the spirit is poured into the lamp. This is afterwards closed by a cork. In the front of the lamp, at *s*, a piece of glass is cemented to afford an opportunity of readily ascertaining how much spirit the spirit-holder *a* contains. The lamp is provided with a copper chimney. The wick must be cut quite level, and must never remain in a charred state. The figure represents a lamp of this sort, drawn according to a scale of one inch and three quarters to a foot. With a lamp such as this, 380 grains of carbonate of soda may be fused in about fifteen minutes, the salt being placed in a platinum crucible of the weight of from 300 to 380 grains, and large enough to contain an equal weight of water. A lamp which is incapable of effecting the fusion of at least 180 grains of carbonate of soda is unfit for use. The experimental chemist should possess two lamps of this description; one for fusing, and another for other experiments. In the latter case, the rods which support the lamp may be strong, but for the other lamp the rods must be as thin as possible, in order that they may not carry away too much of the heat.—TRANSLATOR.

luble or difficultly soluble in water. Very often, in the latter case, it is only the acid, and not the neutral, compounds, which are insoluble or difficultly soluble in water. Compounds of this description are those of potash, with peroxide of uranium, peroxide of tin, protoxide of antimony, antimonious acid, antimonic acid, oxide of tellurium, titanic acid, and silicic acid.

The best reagents for detecting potash in solutions, are chloride of platinum and tartaric acid. Hydrofluosilicic acid follows next. Sulphate of alumina is not so good. As chloride of platinum behaves towards ammoniacal salts in the same manner as towards potash salts, it is necessary, when using this reagent, to have previously ascertained that the substance under examination contains no ammonia.

When potash, or its salts, is combined with much organic matter in solutions, the presence of potash can be detected by tartaric acid, and by chloride of platinum, even in liquids which are very deeply coloured. When an organic substance of a pasty or even solid consistence is to be tested for potash, it can be macerated in water, or in diluted muriatic or nitric acid; but if the quantity of the substance be not considerable, it is best to char it in a Hessian crucible at a moderate heat, and to treat the charred mass with water or muriatic acid. The presence of potash can then be detected, in the filtered solution, by the reagents above cited.

II. SODA.

Soda, in a pure state, and when solid, has much similarity with pure potash. Its solution in water differs from that of potash, in its behaviour towards reagents. Neither a concentrated solution of *Tartaric Acid* when added in excess, nor of *Chloride of Platinum*, or of *Carbazotic Acid*, produces any precipitate. In the last case, however, the solution of soda must not be too concentrated. Even a solution of *Sulphate of Alumina,* on being added to a solution of soda which has been saturated by an acid, produces no crystals of alum. *Hydrofluosilicic Acid* produces, however, in solutions of soda which are not too dilute, a slight voluminous and opalescent precipitate.

Before the *Blowpipe,* soda can be distinguished from potash as follows: A glass of borax in which pure oxide of nickel has been dissolved, is not deprived of its brown colour by the addition of soda. But it can be far better distinguished from potash by the colour which it communicates to the outer blowpipe flame. When a little soda is fused on a platinum wire bent into an ear, and the point of the inner flame is directed upon the bead, the outer flame is coloured strongly yellow, the flame produced resembling that of a candle when burning quietly. This colouring is produced even when much potash is mixed with the soda.

In the salts of soda, which are soluble in water, the soda is distinguished from potash, in the same manner as when in a pure state. The soda salts in a solid state are best distinguished before the blowpipe, by the strong yellow colour which they communicate to the outer flame. When the soda salt is mixed with a potash salt, merely a yellow colour is given to the outer flame, but the yellow colour is rendered weaker by the presence of a considerable quantity of potash salts. When, however, chloride of sodium is mixed with so much chloride of potassium that only $\frac{1}{25}$ or $\frac{1}{30}$ of the former is present, then, according to v. KOBELL (KASTNER'S Archiv. T. XIII. p. 390), the reaction of potash disappears, and only that of soda is exhibited.

The neutral soluble salts of soda are for the most part not decomposed by ignition. With the exception of nitrate of soda, they may all be ignited, provided atmospheric air be excluded.

The crystallised neutral salts of soda, when they contain water, which most of them do, effloresce in the air. This is particularly the case with the sulphate, phosphate, arseniate, and carbonate. The efflorescence occurs in a very inferior degree with the borate, and not at all with the nitrate of soda, nor with the chloride nor fluoride of sodium: the reason of this is, that the three last contain no water of crystallisation.

Of the solutions of the neutral salts of soda, those of the sulphate and nitrate of soda, and of the chloride, bromide, and iodide of sodium, are without action on litmus paper. The solutions of the neutral phosphate, arseniate, borate, and carbonate of soda, and of fluoride and sulphuret of sodium, turn the red litmus paper blue.

Soda produces with very few acids, salts which are insoluble or very difficultly soluble in water. In these salts, the presence of soda is commonly as difficult of detection as the presence of potash in the insoluble or difficultly soluble salts of potash. The acids with which soda produces insoluble or difficultly soluble salts, are the same that produce similar salts with potash. They have been named at page 51.

Soda, in the soluble soda salts, is particularly discriminated, by ascertaining first, that the solution contains an alcali, and secondly, that it affords no precipitate with solutions of chloride of platinum and tartaric acid. But the soda is detected in the safest manner by the yellow colour communicated to the blowpipe flame by the solid salt. If the operator believes that a solution contains both potash and soda, it is best to test a portion of the solution with chloride of platinum, and after the presence or absence of potash has been thus determined, to evaporate another portion of the solution to dryness, and to treat the residue before the blowpipe. If the reaction of the chloride of platinum indicate the presence of potash, and the residue tinges the outer flame of the blowpipe of a violet colour, then potash alone is present. If, on the contrary, the outer blowpipe flame receives a yellow colour from the residue, then both potash and soda are present.

To detect soda, or its salts, in solutions which contain much organic matter, it is necessary to proceed as follows: The solution is evaporated to dryness, and the dry residue, particularly if the quantity be very considerable, is charred in a Hessian crucible by a moderate heat. The charred mass is then macerated in water or muriatic acid, and the solution is filtered and evaporated to dryness. The presence of soda is then detected in the dry residue by the method described above. A pasty or solid organic substance in which the presence of a considerable quantity of soda is suspected, is to be charred and lixiviated precisely in the same manner.

III. LITHIA.

When lithia is pure, it is white and crystalline. It is sparingly soluble in water, and does not become moist in the air. It fuses at a feeble red heat.

The solutions of the lithia salts which are soluble in water, behave towards reagents as follows:

A concentrated solution of *Carbonate of Soda* produces, even in very concentrated solutions of lithia salts, no immediate precipitate. After a considerable time, however, an inconsiderable granular precipitate of sparingly soluble carbonate of lithia is produced.

A solution of *Phosphate of Soda* produces no precipitate in the solutions of lithia salts, even after a long time; but if ammonia be added to the mixture, a strong precipitate is soon produced. If the mixture is boiled before the ammonia is added, a precipitate is also produced. If a solution of lithia, to which a solution of phosphate of soda has been added, be evaporated, the solution becomes troubled during the evaporation: when the whole has been evaporated to dryness, and the residue treated with water, the insoluble or sparingly soluble double phosphate of soda and lithia remains undissolved.

A solution of *Phosphate of Potash* produces no precipitate in the solutions of lithia salts, even after a long reposure; neither is any precipitate produced when the mixture is boiled. If the solution be evaporated to dryness, and the dry residue be treated with water, the whole of it redissolves.—If, however, the solution of a lithia salt be treated with a solution of sulphate of potash, and then with ammonia, a strong precipitate is formed by degrees.

A solution of *Tartaric Acid*, added in excess, produces no precipitate, even in very concentrated solutions of lithia salts.

A solution of *Oxalic Acid* also produces no precipitate.

Hydrofluosilicic Acid produces no precipitate.

A solution of *Chloride of Platinum* produces in the spirituous solutions of lithia salts a troubling which is so extremely inconsiderable as to be scarcely observable. If the solution of lithia be slightly diluted, the troubling is indiscernible.

A solution of *Sulphate of Alumina* produces no crystals in the concentrated solutions of lithia, not even when those precautions are taken which have been spoken of in the case of the potash salts (page 48.)

Before the *Blowpipe*, the lithia in salts of lithia can be very well detected. When a portion is melted upon the end of a platinum wire bent into a ring, and the melted mass is placed at the point of the inner flame, then the outer flame acquires a beautiful and very strong carmine red colour. This colouring of the flame is effected in the most striking manner by the chloride of lithium. When the lithia salt is mixed with a potash salt, then the red colour alone is produced before the blowpipe, and the presence of potash, even when the assay contains more potash than lithia, cannot be detected by its behaviour before the blowpipe.—When, on the contrary, the lithia salt is mixed with a soda salt, then only the reaction of the soda is observable, and the outer flame, even when an excess of lithia is present, acquires merely a yellow colour. This is also the case when a lithia salt contains both potash and soda salts.

Most of the neutral soluble salts of lithia can be ignited without undergoing decomposition (if atmospheric air be excluded, nearly all but the nitrate of lithia).—They fuse at a lower temperature than the corresponding salts of potash and soda.

The solutions of lithia salts act upon litmus paper in the same manner as the corresponding potash and soda salts.

The spirituous solutions of lithia salts burn with a beautiful carmine red flame. The lithia salts which are insoluble in spirits of wine, can still be made to give this colour to its flame. For this purpose, they must be pulverized, mixed with the liquid, and stirred with a glass rod while the spirit burns. The colour is most distinct when the spirits of wine is nearly all consumed.

Lithia produces salts which are insoluble or sparingly soluble in water with the same acids that produce similar compounds with potash and soda. The presence of lithia can be detected in these salts, in the same manner as the presence of potash in the corresponding potash salts (page 50). Independent, however, of these compounds, lithia produces salts which are insoluble or sparingly soluble in water, with other acids which with potash or soda, produce easily soluble salts. Such acids are carbonic acid, and more particularly phosphoric acid, if the action of the latter be assisted by the presence of soda. In the double salt of phosphate of soda and phosphate of lithia, the lithia is not easy of detection. This salt fuses before the blowpipe, and that with still greater facility, if previously mingled with soda, and then held either by a platinum wire bent into an ear, or upon platinum foil. The fused mass is clear, but on cooling becomes opaque and crystalline. If the double salt be fused upon charcoal, it is absorbed.—The earthy phosphates, such as phosphate of lime and of magnesia, which are liable to be mistaken for this double salt, are distinguished from it by not entering into fusion when heated with soda on platinum foil or wire. But if the operator employs a very great excess of soda in this experiment, then the whole melts together, yet in that case, the undissolved earthy phosphate can be distinctly perceived in the fused mass. When the earthy phosphates are fused with soda upon charcoal, the latter is absorbed by the support, while the former remain alone upon its surface.

The presence of lithia, in solutions of the salts of lithia, is best determined as follows: The operator first assures himself, by the addition of a solution of carbonate of potash or carbonate of soda, that the salt in solution is actually an ne salt, which point is determined if this test, on being o a not very concentrated solution of the compound, produces no precipitate. In the next place, if the solution be not troubled by solutions of tartaric acid and chloride of platinum, the absence of potash is determined. If farther, the solution, on being mixed with a solution of phosphate of soda and ammonia, produces, after some time, a strong precipitate, the presence of lithia is determined, and that substance is hereby distinguished, more particularly from soda, but also from potash. Finally, lithia can be sufficiently discriminated from the other two alcalies by its behaviour before the blowpipe.

IV. AMMONIA.

Pure ammonia dissolved in water, possesses a strong and peculiar smell, by which it can easily be recognised. When the quantity of free ammonia in water is so extremely small, that its presence can no longer be detected by the smell, it can be easily detected by holding a glass rod moistened with pretty strong but not fuming muriatic acid, over the surface of the liquid: there is then a production of white clouds over the liquid, even when a very small quantity of ammonia is present. If the quantity of ammonia be considerable, so that it can even be detected by the smell, the production of the white clouds is much more striking. The glass rod may also be moistened with nitric acid or acetic acid, but muriatic acid is more sensible when an extremely small quantity of ammonia is to be detected.

The solution of ammonia has a very caustic taste, and when concentrated, dissolves the skin of the tongue. It colours reddened litmus paper strongly blue. If ammonia be preserved in bottles which are not well protected from atmospheric air, an inconsiderable portion of it is converted, after a very long time, into carbonate of ammonia.

A solution of *Chloride of Platinum* or of *Sulphate of Alumina* behaves towards a solution of ammonia precisely as towards a solution of potash (page 47).

A concentrated solution of *Tartaric Acid* produces in the solution of ammonia, when it is concentrated, a crystalline precipitate of bitartrate of ammonia. If, however, the solution be very dilute, no precipitate is formed.—This precipitate is far more soluble in water than the bitartrate of potash.

A solution of *Carbazotic Acid* produces in the solution of ammonia, when it is not too concentrated, no precipitate.

Hydrofluosilicic Acid produces in the solution of ammonia a strong precipitate of silicic acid, but only such a quantity of hydrofluosilicic acid must be added as leaves ammonia in excess; in the opposite case, no precipitate is produced.

In the salts of ammonia which are soluble in water, the presence of ammonia is detected by solutions of *Chloride of Platinum* and *Sulphate of Alumina*, precisely the same as potash is detected in the corresponding potash salts (page 48). *Tartaric Acid*, added in excess to concentrated solutions of ammonia salts, produces either a far smaller precipitate than in the solutions of the corresponding potash salts, or else no precipitate whatever. *Carbazotic Acid* behaves in the same manner.—*Hydrofluosilicic Acid* produces no precipitate in solutions of ammoniacal salts.

Nearly all the salts of ammonia are totally volatilizable by heat. The compounds formed by ammonia with sulphuric, nitric, arsenic, carbonic, muriatic, hydrobromic, hydrofluoric, and hydrosulphuric acids, volatilize without leaving a remainder; but of all these salts, only the carbonate and muriate of ammonia can be sublimed in contact with atmospheric air, without suffering decomposition. The phosphate and borate of ammonia, on being ignited in glass vessels, leave a remainder. This is also the case with hydrofluate of ammonia, when it is heated in vessels of glass, which it strongly attacks. In platinum vessels, it volatilizes completely.

When dry ammoniacal salts and caustic alcalies or alcaline earths are triturated together, the well-known and peculiar odour of ammonia, is rendered immediately perceptible. Carbonates of alcalies and of alcaline earths operate in the same way, excepting that the ammoniacal odour is, in the latter case, weaker. The like effect is produced, by the mixture of the concentrated solutions of ammoniacal salts with those of caustic and carbonated alcalies and alcaline earths. When the quantity of ammonia or carbonate of ammonia thus disengaged is too small to be clearly distinguished by the smell, its presence is infallibly made known by bringing a glass rod moistened with pretty strong but not fuming muriatic acid over the surface of the liquid or the mixture wherein the supposed ammoniacal salt is mingled with the alcali or alcaline earth; for, hereby a white cloud is produced when but a very slight trace of ammonia is present.

Ammonia, like the other alcalies, produces with some acids, salts which are insoluble or very sparingly soluble in water. In these compounds, however, the presence of ammonia is detected by the application of heat alone, by which the ammonia is expelled. To determine with certainty the presence of ammonia in these compounds, a portion is ignited in a glass tube closed at one end; and, during the ignition, a glass rod moistened with muriatic acid is brought to the open end of the glass tube.

Ammonia, in the soluble ammoniacal salts, is best detected by the ammoniacal odour produced by the action of caustic potash. This serves to distinguish it from the other alcalies.—On account of the action which takes place with solutions of chloride of platinum and sulphate of alumina, ammoniacal salts are liable to be mistaken for salts of potash.

When ammonia in a free state is contained with much organic matter in solutions or pasty mixtures, its presence is detected by the smell. When the salts of ammonia are thus circumstanced, the solution, or pasty mass, is treated with a concentrated solution of potash, and the whole is warmed, upon which the odour of ammonia is soon perceptible. The operator proceeds in the same manner when dry organic substances are mingled with ammoniacal salts. If the solution be too dilute, it must be concentrated by evaporation before it is treated with potash.

V. BARYTES.

Pure barytes is of a greyish white colour and very friable. When a little water is poured over it, heat is produced, and the barytes falls into a white powder. With a larger quantity of water, it forms a crystalline mass, which, if the barytes be pure, is completely soluble in hot water. The concentrated solution of barytes in hot water, deposits on cooling, if the atmosphere is excluded, crystals of hydrate of barytes.—The solution of barytes possesses a caustic taste, and colours reddened litmus paper strongly blue. When exposed to air, it soon attracts carbonic acid, and becomes covered with a film of carbonate of barytes. This is insoluble in water, and gradually sinks to the bottom of the solution. In proportion as it subsides, another film of carbonate of barytes is formed in the same manner, and finally the whole of the barytes is converted into carbonate of barytes and precipitated.—The hydrate of barytes dissolves in a very large quantity of alcohol.—Pure barytes does not fuse at a red heat, but the hydrate of barytes fuses at a red heat with facility.

The solution of barytes in water, after being saturated with an acid, as, for example, with muriatic acid, behaves like the solutions of such barytic salts as are easily soluble in water.

The most diluted solutions of barytes, when mixed with a little diluted *Sulphuric Acid,* or the solution of a *Sulphate,* give a white precipitate, which does not redissolve on the addition of a free acid. For this proof, it is best to use muriatic or nitric acid.

Hydrofluosilicic Acid produces in barytic solutions, after a while, a crystalline precipitate, which is almost completely insoluble in free muriatic or nitric acid.

A solution of *caustic Potash* produces, in concentrated solutions of barytic salts, a voluminous precipitate, which, on the addition of a considerable quantity of water, almost entirely disappears, provided that the potash employed be free from carbonic acid. After some time, the absorption of carbonic acid from the atmosphere produces in the first place a skin, and subsequently a precipitate.

Caustic Ammonia produces no precipitate in barytic solutions. If, however, the solution of a barytic salt be mingled with caustic ammonia, and allowed to stand a long time (for some days) exposed to the air, there is a production of carbonate of barytes which fixes itself very firmly to the sides of the vessel in the state of crystalline sandy grains; these, on being subjected to the action of a free acid, effervesce, and disengage carbonic acid gas. When the carbonate of barytes has been thus deposited, the liquid retains no more barytes in solution.

A solution of *Carbonate of Potash* forms in solutions of barytic salts a white precipitate, which dissolves in free acids. If the quantity of the precipitate be pretty considerable, its solution in acids is accompanied by effervescence; if it is but small, no effervescence arises, because the disengaged carbonic acid dissolves in the liquor.

A solution of *Bicarbonate of Potash* produces, in concentrated solutions of barytic salts, a white precipitate, which is only slightly soluble in a large quantity of water, but dissolves with strong effervescence in free acids.

A solution of *Carbonate of Ammonia* produces a white precipitate in barytic solutions.

A solution of *neutral Phosphate of Soda* produces, in barytic solutions, a white precipitate, the quantity of which is not augmented on the addition of caustic ammonia, and which is soluble in free muriatic or nitric acid.

A solution of *Oxalic Acid*, or *Binoxalate of Potash*, gives no precipitate, even in pretty concentrated neutral solutions of barytic salts. It is only when the solutions are very concentrated, and not then till after some time, that a precipitate appears. But upon the addition of caustic ammonia, there follows a white precipitate. Yet, even in that case, if the barytic solution be very dilute, no precipitation occurs.

A solution of neutral *Succinate of Ammonia* produces, in concentrated solutions of barytic salts, an immediate precipitate. In diluted solutions, the precipitate does not appear till after some time. This precipitate is soluble in acids.

Hydrosulphuret of Ammonia, as well as solutions of *Prussiate of Potash* and *red Prussiate of Potash*, produce no precipitates in barytic solutions.

Of the barytic salts which are soluble in water, chloride of barium alone can be heated to redness, in contact with the air, without suffering decomposition.—The solutions of the neutral barytic salts, that of sulphuret of barium excepted, have no action on litmus paper. The solution of sulphuret of barium turns reddened litmus paper blue.

The salts formed by barytes with most acids, as with sulphuric acid, phosphoric acid, arsenic acid, boracic acid, carbonic acid, &c., are either insoluble or sparingly soluble in water. Nearly the whole of these salts dissolve, however, in free muriatic or nitric acid: the sulphate of barytes alone is insoluble in these acids. The presence of barytes, in these acid solutions, can consequently be detected by the addition of diluted sulphuric acid, which produces a precipitate. On account of this property, barytes can only be mistaken for strontian, or, in some cases, for lime.—To detect the presence of barytes, in sulphate of barytes, a portion of the pulverised substance is boiled in water, by which means the operator convinces himself of its utter insolubility in water. It is then boiled with a solution of carbonate of potash or soda, and filtered. The insoluble remainder is treated with muriatic acid, the solution is filtered, and then tested with diluted sulphuric acid, which produces a precipitate.—The method of distinguishing sulphate of barytes from sulphate of strontian, both of which substances are acted upon in the same manner when boiled with carbonate of alcali, will be described under the head of Strontian.

Before the *Blowpipe*, barytes and its salts cannot be discriminated from other substances with certainty.

Barytes in solution is particularly distinguished from alcalies in solution, by the production of white precipitates when tested with carbonate of potash, and diluted sulphuric acid.

When barytic salts are contained in solutions with much organic matter, a precipitate of sulphate of barytes is produced by diluted sulphuric acid, even when the liquids are very darkly coloured. The solutions must be previously acidulated by muriatic or nitric acid. When the analyst has obtained a precipitate by proceeding in this manner, it is proper that he convince himself that barytes is really contained in it. The precipitate must with this view be decomposed in the manner which has been described above. When barytes is to be detected in pasty or solid organic substances, they must be digested in water acidulated by nitric acid; the solution must be filtered, and then tested with diluted sulphuric acid.—When the compound for examination contains sulphate of barytes mingled with pasty or solid organic substances which are not soluble in pure water, it is best to proceed as follows: The whole mass is gradually and cautiously heated in a Hessian crucible, and the heat is finally increased to such a degree that the charcoal produced by the organic matter reduces the sulphate of barytes to sulphuret of barium. When the ignited mass is cold, it is boiled with water. The solution thus obtained is decomposed by muriatic acid, and the presence of barytes is then easily detected by the addition of diluted sulphuric acid. If the organic substances with which the sulphate of barytes is mingled, are soluble in water, it is best to separate them by solution, and then to examine the sulphate of barytes in the manner already described.

VI. STRONTIAN.

Strontian, in a pure state, is very similar in its properties to barytes. The same may be said of the hydrate of strontian, excepting that this is more sparingly soluble in water than the hydrate of barytes. The aqueous solution of strontian has consequently a less caustic taste; but in other respects the solutions of the two earths behave much in the same manner.

The solution of strontian, after being acidulated by an acid, for example, by muriatic acid, behaves in the same manner as solutions of the salts of strontian which are soluble in water.

Solutions of strontian salts give, with diluted *Sulphuric Acid*, or with solutions of *Sulphates*, a white precipitate, which is insoluble in diluted free acids. Even a small quantity of a strontian salt produces a white precipitate with sulphuric acid; but the precipitate does not then form till after some time. The resulting sulphate of strontian is, however, not so insoluble in water as the sulphate of barytes. Supposing the solution of a strontian salt to have been decomposed by sulphuric acid, not completely however, but in such a manner as to leave a portion of strontian still in solution; and supposing, farther, the whole to have been suffered to repose some time, and then to have been filtered, the clear liquid, furnished by the filtration, is capable of affording a slight white precipitate, on being tested with the solution of a salt of barytes. In this manner, therefore, can barytes and strontian be discriminated.

Hydrofluosilicic Acid produces no precipitate in solutions of strontian, even after a long time.

Solutions of *Potash* and *Ammonia, Carbonate* and *Bicarbonate of Potash, Carbonate of Ammonia,* and *Phosphate of Soda,* behave towards strontian solutions exactly as towards barytic solutions.

A solution of *Oxalic Acid,* or of *Binoxalate of Potash,* troubles the neutral solutions of strontian salts; if they are very dilute, the opalescence does not occur immediately, but only after some time. The precipitate is very considerably augmented upon the addition of caustic ammonia. When a strontian solution gives no immediate precipitate with oxalic acid, on account of being too dilute, the addition of ammonia causes the instant formation of the precipitate.

A solution of neutral *Succinate of Ammonia* produces no precipitate in solutions of neutral salts of strontian. If, however, the solutions be concentrated, a precipitate is produced after a considerable time: it never forms immediately. The precipitate is soluble in acids. This reagent serves to distinguish the salts of strontian from the salts of barytes.

Hydrosulphuret of Ammonia, as well as solutions of *Prussiate of Potash,* and *Red Prussiate of Potash,* occasion no precipitation in solutions of strontian.

The soluble salts of strontian agree, in their relation towards heat, with the salts of barytes.—The solutions of the two earths agree also in their action on litmus paper.

That which peculiarly serves to distinguish the soluble strontian salts from the corresponding barytic salts is, that when they are dissolved in alcohol, or when, not being soluble therein, they are added to it in a pulverised state, the alcohol, on being inflamed, burns with a carmine red flame; the colour being particularly observable when the mixture is stirred, and when the alcohol is nearly all burnt.

Strontian produces compounds which are either insoluble or sparingly soluble in water, with most of the acids with which barytes produces such compounds. These compounds, like those produced by barytes, dissolve in free muriatic or nitric acid, with the exception of the sulphate of strontian, which is insoluble in acids. To discriminate between sulphate of strontian and sulphate of barytes, which substances have much similarity, the operator decomposes the compound, by boiling it with a solution of carbonate of potash or of soda. He then treats the insoluble remainder with muriatic acid, dilutes the acid solution with water, filters it, and adds hydrofluosilicic acid: if the compound consist of sulphate of strontian, no precipitate is produced.—The muriatic acid solution can also be evaporated to dryness, the residue be covered with alcohol, and the alcohol be inflamed: the presence of strontian is denoted by the carmine red colour of the flame.

Before the *Blowpipe,* the presence of strontian is distinctly indicated by only some of the salts of strontian. Sulphate of strontian, in splinters of crystals, held by the platinum forceps at the point of the inner blowpipe flame, communicates, after a long blast, a distinct but not strong carmine red colour to the outer flame. The colour is scarcely to be observed in clear daylight. When chloride of strontian is heated on a platinum wire bent to a ring, and placed at the point of the inner flame, the whole blowpipe flame acquires a strong carmine red colour at the first moment. As soon, however, as the salt is fused, the red colour disappears, so that the blowpipe serves to distinguish chloride of strontian from chloride of lithium. The presence of chloride of barium in the chloride of strontium prevents the production of the carmine red flame.

Strontian in solution is distinguished from solutions of alcaline salts precisely by the same means as barytes is distinguished therefrom. It is distinguished from barytes by its behaviour towards hydrofluosilicic acid, and also by the circumstance that the salts of barytes have not the property of communicating a red colour to the flame of burning alcohol.

When strontian is mingled with much organic matter, the mixture must be treated in the same manner as a mixture of barytes and organic matter.

VII. LIME.

Lime in a state of purity is of a white colour, and very friable. When a little water is thrown upon it, it becomes very hot, and falls to a white powder of a much greater volume than that of the lime employed. If still more water be added to the resulting hydrate of lime, it forms a milky mixture. A very considerable quantity of water is necessary to dissolve a small quantity of hydrate of lime. The solution possesses a slightly caustic taste, and colours reddened litmus paper blue. It attracts carbonic acid from the atmosphere, and produces a superficial film of insoluble carbonate of lime. This film, after some time, falls to the bottom of the solution, but is constantly succeeded by a new film, until, in this manner, the dissolved lime is wholly converted into carbonate of lime, and completely precipitated from the solution.—Both pure lime and hydrate of lime are infusible.

The solution of lime in acids, behaves like the solutions of those salts of lime which readily dissolve in water.

In diluted solutions of calcareous salts, diluted *Sulphuric Acid*, and solutions of *Sulphates*, produce no precipitate. If the solution of the calcareous salt be less dilute, sulphuric acid forms a precipitate, if not immediately, yet after some time. In concentrated solutions of the calcareous salts, sulphuric acid produces an immediate precipitate, which is far more bulky than that of sulphate of strontian or sulphate of barytes, but is not remarkably soluble in diluted muriatic or nitric acid. If a calcareous solution is decomposed by diluted sulphuric acid, in such a manner as to leave a portion of the calcareous salt still in solution, and the whole is allowed to repose for some time before filtration, the filtered liquor affords a precipitate with solutions of salts of strontian or barytes.

Hydrofluosilicic Acid occasions no precipitation in calcareous solutions.

Solutions of *Potash* and *Ammonia*, *Carbonate* and *Bicarbonate of Potash*, *Carbonate of Ammonia*, and *Phosphate of Soda*, behave with calcareous solutions in the same manner as with barytic and strontian solutions.

A solution of *Oxalic Acid* or *Binoxalate of Potash* produces, even in very dilute neutral calcareous solutions, a white precipitate, which, after long reposure, and especially after the addition of caustic ammonia, to saturate the free acid, considerably augments in quantity. This precipitate dissolves easily in free muriatic or nitric acid; but in acetic acid, even when concentrated, it is but slightly soluble.—Supposing the solution of a barytic or strontian salt to have been decomposed by a solution of oxalic acid or of binoxalate of potash, in such a manner as to leave an excess of the barytic or strontian salt in solution, and supposing the whole to have been suffered to repose so long that the precipitate ceases to be augmented, the solution separated therefrom by filtration, produces with the solution of a calcareous salt, a precipitate. Hereby, can a soluble barytic or strontian salt be distinguished from a salt of lime.

A solution of neutral *Succinate of Ammonia* produces no precipitate in neutral solutions of the salts of lime; but, if the solutions of lime be very concentrated, crystals of succinate of lime appear after a considerable time.

Hydrosulphuret of Ammonia, as well as solutions of *Prussiate of Potash* and *Red Prussiate of Potash*, form no precipitate in calcareous solutions.

The soluble salts of lime behave, when ignited, like the soluble salts of barytes.—With litmus paper also, solutions of both earths act alike.

When alcohol is poured over the soluble calcareous salts, and set on fire, it burns with a red coloured flame, very similar to that produced when salts of strontian are thus treated. The salts of lime cannot, in consequence, be distinguished from strontian salts by this experiment, although it serves on the other hand to distinguish them readily from barytic salts.

Lime produces salts which are insoluble or sparingly soluble in water, with the same acids with which barytes and strontian produce such compounds; and the resulting salts, like those produced by the two latter earths, are soluble in free muriatic or nitric acid: but the sulphate of lime, like the sulphates of barytes and strontian, is insoluble in these acids. In the acid solutions of calcareous salts, the presence of lime can be detected by sulphuric acid, but the solutions must not be too much diluted. This reagent produces a precipitate, if not immediately, yet after some time: its production is facilitated by the addition of alcohol to the solution. To distinguish precipitated sulphate of lime from precipitated sulphate of barytes or sulphate of strontian, it is necessary to proceed as follows: The precipitate is well edulcorated, and then boiled in a considerable quantity of water. The solution is filtered, and divided into two portions: one portion is mixed with a solution of chloride of barium, and the other with a solution of an oxalate. If, in both cases, a white precipitate be produced, and that afforded by the chloride of barium be insoluble in muriatic acid, then the base of the sulphate, is lime.

Before the *Blowpipe*, the presence of lime can be distinctly detected in but few of the calcareous salts. The characteristic is the same as the characteristic of strontian in the strontian salts. Chloride of calcium, when heated on a platinum wire bent into an ear, behaves in the same manner as chloride of strontian; that is to say, it communicates a carmine-red colour to the outer flame. The colour is, however, less strikingly exhibited by the lime-salt than by the strontian salts. When the chloride of calcium has been fused, the colouring of the flame is no longer perceptible. The presence of chloride of barium in the chloride of calcium hinders the production of the carmime-red flame. Pure lime and carbonate of lime produce a very powerful light when exposed to the blowpipe flame.

Solutions of calcareous salts are distinguished from solutions of alcaline salts, precisely in the same manner as solutions of barytic salts. Lime is distinguished from barytes by its behaviour with both hydrofluosilicic acid and sulphuric acid; it is distinguished from strontian by its behaviour with sulphuric acid.

When the solution of a salt of lime is mingled with so much organic matter, as to be very deeply coloured, the best way to detect the lime, is to mix the solution with a solution of commercial superoxalate of potash, and to add a little ammonia. Should the solution be very acid, it must previously be neutralised by ammonia; should it be very alcaline, it must previously be neutralised by muriatic acid. By this means, oxalate of lime is precipitated, often with a very dark colour. The precipitate is dried and ignited. The resulting carbonate of lime is dissolved in muriatic acid, and the presence of lime is detected in the solution. When lime, or a salt of lime, is mingled with solid or pasty organic substances, it is best to treat the mass with water acidulated by nitric acid. The solution is filtered, and the clear liquor is tested for lime in the manner described above.—When sulphate of lime is mingled with solid or pasty organic substances which cannot be dissolved by pure water, the mass must be treated in the same manner as if it contained sulphate of barytes. The operation which it is necessary to perform, has been described at page 63.

VIII. MAGNESIA.

Pure magnesia is a white powder, which is infusible by heat, and pretty nearly insoluble in water. If laid upon reddened litmus paper and moistened, it changes the colour to blue. No heat is produced by moistening it with water.

The neutral solution of magnesia behaves like solutions of the easily soluble salts of magnesia.

Sulphuric Acid produces no precipitate in the concentrated solutions of the salts of magnesia.

Neither does *Hydrofluosilicic Acid* occasion precipitation.

A solution of *Potash* produces, in solutions of neutral magnesian salts, a voluminous flocculent precipitate, which does not disappear when the liquid is diluted with water. If the magnesian solution has previously been mingled with a solution of muriate of ammonia, it produces a much smaller precipitate on the addition of potash. Even so, the precipitate at first produced by potash, mostly disappears, when a solution of muriate of ammonia is added. If the whole be then boiled, a precipitate is invariably formed, unless there be a deficiency of potash.

Ammonia produces, in neutral magnesian solutions, a bulky precipitate, which, on the addition of a solution of muriate of ammonia, wholly disappears. When a solution of muriate of ammonia, and then a solution of ammonia is added to a neutral solution of magnesia, no precipitate is formed, unless the muriate of ammonia is added in too small a proportion. When the solution of a magnesian salt is not neutral, but contains free acid, it gives also no precipitate when an excess of ammonia is added, except the quantity of free acid be too inconsiderable to produce a sufficient quantity of ammoniacal salt.

A solution of *Carbonate of Potash* produces, in neutral magnesian solutions, a voluminous precipitate, which completely disappears when a solution of muriate of ammonia is added. No precipitate is produced by carbonate of potash, if, previous to its addition, the magnesian solution be mingled with a solution of muriate of ammonia. In both cases, however, if the solution be boiled, and carbonate of potash be added in sufficient quantity, a voluminous precipitate is formed. When the solution of the magnesian salt contains much free acid, and at the same time is not too concentrated, it produces no precipitate with carbonate of potash; yet, when the mixture is boiled, a precipitate is formed.

A solution of *Bicarbonate of Potash* produces no precipitate in solutions of salts of magnesia, even though they be concentrated and neutral. But if the mixture be boiled for some time, a precipitate is formed.

A solution of *Carbonate of Ammonia* produces, in magnesian solutions, no precipitate, because the carbonate of ammonia generally contains bicarbonate of ammonia. But if a mixture of the two substances be boiled, a precipitate appears. Upon the addition of muriate of ammonia, this precipitate redissolves.

A solution of *Phosphate of Soda* produces a precipitate in concentrated and neutral solutions of magnesia. In pretty dilute solutions, no precipitate is formed when the mixture is cold; but if it be boiled, a precipitate appears, which does not redissolve when the liquor becomes cold. When a solution of phosphate of soda is mingled with a neutral solution of magnesia, and the mixture is so much diluted that no precipitate appears in the cold, the addition of caustic or carbonated ammonia produces an immediate precipitate.

Solutions of *Oxalic Acid* and of *Binoxalate of Potash* produce no precipitate in neutral magnesian solutions. When the quantity of oxalic acid or solution of oxalate which has been added is inconsiderable, the addition of an excess of ammonia is sufficient to produce a precipitate, even if the magnesian solution has been previously diluted with a large proportion of water. But if the quantity of oxalic acid or of binoxalate of potash which has been added to the magnesian solution be considerable, or if the solution of the magnesian salt was not neutral, but contained free acid, then the addition of an excess of ammonia produces no precipitate, not even in very concentrated solutions.

Hydrosulphuret of Ammonia produces, in magnesian solutions, no precipitate. When a neutral solution of magnesia is precipitated by this reagent, it is because the precipitant contains very much free ammonia.

Solutions of *Prussiate of Potash* and of *Red Prussiate of Potash* produce no precipitate in solutions of magnesia.

Of the magnesian salts which are easily soluble in water, none but the sulphate of magnesia can be ignited in contact with air, without suffering decomposition.—The solutions of the neutral salts of magnesia have no action on litmus paper.

Magnesia produces, with a great number of acids, salts which are insoluble or sparingly soluble in water. Phosphoric acid, arsenic acid, carbonic acid, and boracic acid, all produce salts of this description. These salts are all soluble in sulphuric or muriatic acid. But some of the acid salts, after having undergone ignition, can only be dissolved by being boiled with concentrated sulphuric acid; the acid phosphate of magnesia is a salt of this description. To detect the presence of magnesia in the acid solutions of the salts of magnesia, they must be boiled with an excess of a solution of potash, often for a pretty long time: the magnesia is then precipitated, while the acid with which it was combined, as well as that in which it was dissolved, combine with the potash and remain in solution. The precipitated magnesia is collected and washed. It is then examined before the blowpipe, or instead of that, is dissolved in an acid; for which purpose, muriatic acid or diluted sulphuric acid may be taken, and the solution is examined by tests.

The salts of magnesia can also be detected by igniting a small portion on charcoal before the *Blowpipe*, moistening the ignited assay with a solution of nitrate of cobalt, and again strongly heating it. By this means, the mass is made to acquire a pale red colour, which is not the case with bodies that contain no magnesia. Pure magnesia and carbonate of magnesia, if mixed with water to a paste, and then spread upon charcoal and ignited, acquire the same red colour from solution of cobalt.—The presence of metallic oxides, alcalies, and earths, prevent the reaction of the solution of cobalt. Silicic acid does not prevent it. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 73.)

Magnesia, in neutral solutions, is distinguished from solutions of alcaline salts by producing white precipitates with caustic ammonia and carbonate of potash. It is distinguished from solutions of barytes, strontian, and lime, by caustic ammonia, which produces no precipitate with the three latter earths.

But when the solutions of magnesia are acid, they are distinguished from solutions of potash, soda, and ammonia salts, by producing a white precipitate with a solution of phosphate of soda, after having been supersaturated with ammonia. They are distinguished from solutions of lithia salts, by affording a precipitate with an excess of potash, particularly when the mixture is boiled. From solutions of barytes and strontian, they are distinguished by affording no precipitate with diluted sulphuric acid; and from solutions of lime, by their relation towards oxalic acid.

The presence of non-volatile organic substances can often prevent (or partially prevent) the precipitation of magnesia by alcalies. When, however, even small quantities of magnesia are mixed with large quantities of organic substances, the former can be precipitated from the solutions, by a mixture of phosphate of soda and free ammonia.

IX. ALUMINA.

Alumina in a state of purity is white, but often, when obtained by gently drying the hydrate of alumina, appears yellowish and horny. It is insoluble in water, but readily dissolves in acids, provided it has not been ignited. Ignition renders it difficultly soluble, and in many acids nearly insoluble. After ignition, it is best dissolved by digestion with concentrated muriatic acid, diluted with a very small proportion of water. It can also, in the same case, be dissolved by diluted but warm sulphuric acid. The neutral solution of alumina in acids, behaves, when diluted with water, like the solutions of aluminous salts which are soluble in water.

No free acid, not even hydro-fluosilicic acid, produces a precipitate in solutions of aluminous salts.

A solution of *Potash* produces in neutral aluminous solutions, a bulky precipitate, which entirely redissolves in an excess of potash. In such a solution of alumina in potash, a solution of muriate of ammonia produces a precipitate of alumina.

Ammonia produces in solutions of alumina, a voluminous precipitate, which no excess of ammonia redissolves. The presence of muriate of ammonia does not hinder the production of this precipitate, nor yet of the precipitates produced by the following reagents; on which account, salts of alumina cannot be mistaken for salts of magnesia.

A solution of *Carbonate of Potash* produces, like ammonia, a voluminous precipitate, which is, in this case also, insoluble in an excess of the precipitant. If the solution be concentrated, an effervescence takes place, in consequence of the disengagement of carbonic acid gas.

A solution of *Bicarbonate of Potash* acts in the same manner; the effervescence occasioned by the discharge of carbonic acid gas is in this case, however, much stronger.

A solution of *Carbonate of Ammonia* behaves in the same manner.

A solution of *Phosphate of Soda* produces in neutral solutions of alumina, a voluminous precipitate, which, like the other precipitates, is soluble in acids and in a solution of potash.

Solutions of *Oxalic Acid*, and of *neutral Oxalates*, effect no precipitation in neutral solutions of alumina.

If a solution of alumina be mixed with *Potash*, either caustic or carbonated, and a slight excess of *Sulphuric Acid* be added, then after some time, crystals of alum are formed in the solution. If the solution of alumina be dilute, it must previously be concentrated by evaporation, or the addition of potash and sulphuric acid will produce no crystals of alum.

Solutions of *Prussiate of Potash* and of *Red Prussiate of Potash* produce no precipitates in aluminous solutions.

Hydrosulphuret of Ammonia produces in neutral aluminous solutions, a precipitate of alumina, while sulphuretted hydrogen becomes free. This gas is discharged from very concentrated solutions with effervescence. As this precipitate consists of pure alumina, it is soluble in a solution of potash.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces in neutral aluminous solutions no precipitate; neither is any precipitate produced when sulphuretted hydrogen gas is passed into the solution of alumina in potash.

The neutral soluble salts of alumina redden blue litmus paper. The salts which dissolve in water cannot be ignited without being decomposed.

Alumina produces with a great number of acids, salts which, in a neutral state, are insoluble in water. Phosphoric and arsenic acids give salts of this description. These salts are, previous to ignition, very easily soluble in free muriatic and sulphuric acid, as well as in a solution of potash. The solutions produced by dissolving the phosphate, arseniate, and some other salts of alumina, in acids or in a solution of potash, behave towards reagents nearly in the same manner as a solution of pure alumina. It is therefore very easy to mistake these salts for pure alumina. To distinguish the one from the other, it is necessary to test the compounds for the acids which may be present.

The method of doing this will be described farther on, when we come to treat of the acids.

Before the *Blowpipe*, alumina in a pure state, as well as in most of the compounds of alumina, particularly such as are not easily fusible, can be very well detected. The experiment consists in heating a small portion of the substance on charcoal, then moistening it with a solution of nitrate of cobalt, and again strongly heating it in the blowpipe flame; whereby, a fine blue colour is communicated to the assay, which is not the case with substances that contain no alumina. The fine blue colour appears of a pure blue only in daylight; when seen by candle light, it appears to be dirty violet. (BERZELIUS, *Anwendung des Löthrohrs*, p. 74.)

Solutions of alumina are distinguished from solutions of alcaline salts by producing white precipitate with ammonia;—from solutions of barytes, strontian, and lime, by producing a white precipitate with ammonia, and no precipitate with sulphuric acid, as those earths do (excepting the solution of lime, when too dilute);—and from solutions of magnesia by its behaviour with solutions of potash and muriate of ammonia.

When a solution of alumina contains much organic matter, especially such as cannot be volatilized in an undecomposed state by heat, but suffers decomposition at an elevated temperature, and leaves a large residue of charcoal, the presence of the alumina is often incapable of detection by the usual reagents, even though the solution be not coloured by the organic matter. Ammonia and solutions of carbonate of potash and carbonate of ammonia, are incapable of precipitating alumina from such solutions, even when added in very great excess. Neither can crystals of alum be produced by the addition of potash and sulphuric acid. The presence of alumina in solutions which contain much organic matter can therefore be detected, only by evaporating the solutions to dryness and igniting the residue, to destroy the organic matter. The dry mass left by the ignition, is digested in an acid, as, for example, in muriatic acid or sulphuric acid, and the filtered solution is tested for alumina by the usual reagents.—If alumina be contained in solid or pasty organic substances, these must likewise be destroyed by ignition, and the residue treated in the manner just described.

X. GLUCINA.

Pure glucina has a white colour, and is insoluble in water. It dissolves in acids, yet, after ignition, not without difficulty.

The solution of glucina in acids behaves towards reagents like the solutions of the salts of glucina.

Free acids produce no precipitate in solutions of glucina, not even hydrofluosilicic acid.

A solution of *Potash* produces in solutions of glucina, as in solutions of alumina, a voluminous precipitate which completely redissolves in an excess of potash. A solution of muriate of ammonia, added to a solution of glucina in potash, produces a precipitate of glucina.

Ammonia produces in solutions of glucina a voluminous precipitate, which does not redissolve in an exces of ammonia. The addition of a solution of muriate of ammonia does not prevent the production of this precipitate; neither is muriate of ammonia capable of hindering the reaction of the following reagents.

A solution of *Carbonate of Potash* produces in solutions of glucina, a voluminous precipitate, which redissolves in a great excess of the precipitant.

A solution of *Bicarbonate of Potash* behaves in the same manner.

A solution of *Carbonate of Ammonia* behaves like carbonate of potash, excepting that the precipitated glucina dissolves more easily in carbonate of ammonia than in carbonate of potash.

A solution of *Phosphate of Soda* produces in solutions of glucina, a voluminous precipitate.

Solutions of *Oxalic Acid* and of *Oxalates* produce no precipitate in solutions of glucina.

When *Potash* is added to a solution of glucina, and the solution is slightly supersaturated by *Sulphuric Acid*, no crystals of alum are produced.

Solutions of *Prussiate of Potash* and of *Red Prussiate of Potash* produce no precipitate in solutions of glucina.

Hydrosulphuret of Ammonia produces in neutral solutions of glucina, a precipitate of glucina, which is soluble in a solution of potash.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces no precipitate in solutions of glucina.

Litmus paper is reddened by the neutral solutions of glucina.

The salts of glucina which dissolve in water, are decomposed by ignition.

Glucina produces with a great number of acids, compounds which, in a neutral state, are insoluble in water. These are frequently, like the corresponding compounds of alumina, difficult to be distinguished from pure alumina.

Glucina and most of its compounds, when moistened with solution of nitrate of cobalt and treated in the flame of the *Blowpipe*, do not become blue, but dark grey or black.

Solutions of glucina are distinguished from solutions of alcaline salts, as well as from those of barytes, strontian, lime, and magnesia, in the same manner as solutions of alumina are distinguished from those compounds. Glucina is distinguished from alumina by its behaviour with solutions of alcaline carbonates, particularly with that of carbonate of ammonia. It is farther distinguished by giving no crystals of alum with potash and sulphuric acid, and when in a solid state, by its behaviour with solution of nitrate of cobalt before the blowpipe.

When a solution of glucina contains a great quantity of non-volatile organic substances, the presence of glucina is as difficult of detection by the usual reagents as the presence of alumina under similar circumstances. The only method of proceeding is to evaporate the solution to dryness, to calcine the residue, and to treat the ignited mass with muriatic acid. The presence of glucina can then be detected in the muriatic acid solution.

XI. THORINA.

On account of the great scarcity of thorina, I have had no opportunity of personally examining its properties, or of proving its behaviour towards reagents. What is said here upon the subject, is taken from the memoir on thorina, which has been published by BERZELIUS (POGGENDORFF'S *Annalen*, T. XVI. p. 385).

Thorina in a pure state is colourless. After ignition, it is insoluble in all acids except sulphuric acid, and it is only dissolved in the latter by being heated in a mixture of concentrated sulphuric acid with an equal weight of water. Even when thorina has been ignited with pure or carbonated alcalies, it is still insoluble in muriatic or nitric acid. These acids merely extract the foreign matters with which the thorina may be contaminated, and which cannot be extracted from the earth when it has been ignited without the addition of alcali. Most other oxides which simple ignition renders insoluble in acids, are rendered soluble by ignition with alcalies, in which respect they differ from thorina.—The hydrate of thorina, when in a moist state, dissolves, on the contrary, very easily in acids; but after becoming dry, it dissolves more sparingly and slowly.

A solution of *Potash* produces a gelatinous precipitate in solutions of thorina. This precipitate easily sinks together, and is insoluble in an excess of the precipitant.

Ammonia behaves in the same manner.

Solutions of *Carbonate of Potash* and *Ammonia* produce in solutions of thorina, a precipitate which dissolves in an excess of the precipitant. The solution is effected pretty easily when the solution of the precipitant is concentrated, but with more difficulty when the precipitant is too dilute.

A solution of *Phosphate of Soda* produces in solutions of thorina, a white flocky precipitate, which is insoluble in an excess of phosphoric acid.

A solution of *Oxalic Acid* produces in solutions of thorina, a white, heavy precipitate, which is insoluble in an excess of oxalic acid and soluble in an extremely slight degree in other free and diluted acids.

A solution of *Sulphate of Potash* troubles the solutions of thorina very slowly, but if the solution of sulphate of potash be concentrated and added in excess, the whole of the thorina is finally precipitated, as a double salt.

A solution of *Prussiate of Potash* produces in neutral solutions of thorina, a white heavy precipitate, which is soluble in acids.

A solution of *Red Prussiate of Potash* produces no precipitate in solutions of thorina.

Hydrosulphuret of Ammonia produces in neutral solutions of thorina, a precipitate of hydrate of thorina.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces no precipitate in solutions of thorina.

The salts of thorina which dissolve in water, are decomposed by ignition.—The solutions of many of its salts are precipitated by boiling; for example, the solution of the sulphate is thus acted upon. This reaction does not take place, however, when bases are present with which thorina produces double salts.

Solutions of thorina are distinguished from solutions of alcalies, as well as from those of barytes, strontian, and lime, by giving a precipitate with ammonia; from solutions of magnesia, by its behaviour towards ammonia and hydrosulphuret of ammonia; and from solutions of alumina and glucina, by producing with a solution of potash, a precipitate which does not redissolve in an excess of the precipitant.

XII. YTTRIA.

Pure hydrate of yttria has a white colour, which ignition renders dirty yellow. It easily dissolves in acids.

A solution of *Potash* produces in solutions of yttria, a white, voluminous precipitate, which is insoluble in an excess of the precipitant.

Ammonia behaves in the same manner.

A solution of *Carbonate of Potash* produces in solutions of yttria, a white voluminous precipitate, which is slightly soluble in a great excess of the precipitant.

A solution of *Bicarbonate of Potash* produces in solutions of yttria a white voluminous precipitate, which completely dissolves in a very great excess of the precipitant.

A solution of *Carbonate of Ammonia* behaves in the same manner.

A solution of *Phosphate of Soda* produces in solutions of the neutral salts of yttria, a white precipitate, which is soluble in muriatic acid, but can be again precipitated by boiling the acid solution.

A solution of *Oxalic Acid* produces even in slightly acid solutions of yttria a voluminous white precipitate, which dissolves in muriatic acid.

A solution of *Sulphate of Potash* produces a precipitate in solutions of yttria. The precipitate does not appear till after a considerable time, and is completely redissolved on the addition of water, even if the water contain sulphate of potash in solution.

A solution of *Prussiate of Potash* produces a white precipitate in solutions of yttria.

A solution of *Red Prussiate of Potash* produces no precipitate in solutions of yttria.

Hydrosulphuret of Ammonia produces in neutral solutions of yttria, a precipitate of yttria.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces no precipitate in solutions of yttria.

The solutions of the neutral salts of yttria redden litmus paper.

The salts of yttria which are soluble in water, are decomposed by ignition.

Before the *Blowpipe*, yttria, which behaves in the same manner as glucina, cannot be well distinguished from similar earths.

Solutions of yttria are distinguished from solutions of alcalies, barytes, strontian, lime, and magnesia, in the same manner as solutions of alumina are distinguished from those substances. From solutions of alumina and glucina, those of yttria are distinguished by producing with a solution of potash, a precipitate which does not redissolve in an excess of potash. Yttria and thorina are distinguished by the double salt produced by sulphate of potash, which if it contain thorina, is insoluble in a saturated solution of sulphate of potash, but soluble if it contain yttria.

The presence of non-volatile organic substances in its solutions, prevents the precipitation of yttria by alcalies.

XIII. OXIDES OF CERIUM.

a. PROTOXIDE OF CERIUM.

When pure and in the state of hydrate, the protoxide of cerium is white, but it becomes yellowish in the air in consequence of the absorption of oxygen. When ignited in contact with air, it becomes brick-red, being converted into peroxide of cerium. The protoxide of cerium readily dissolves in acids: when heated with muriatic acid, it almost always dissolves under a feeble disengagement of chlorine. Yet this is a property, not of the protoxide of cerium but of the peroxide, which is always contained in the protoxide in consequence of the facility with which the latter, when in a moist state, becomes oxidised in the air.

A solution of *Potash* produces in solutions of protoxide of cerium, a white voluminous precipitate, which is insoluble in an excess of the precipitant.

Ammonia behaves in the same manner.

A solution of *Carbonate of Potash* produces in solutions of protoxide of cerium a white voluminous precipitate, which is very slightly soluble in an excess of the precipitant.

A solution of *Bicarbonate of Potash* or of *Carbonate of Ammonia* behaves in the same manner.

A solution of *Phosphate of Soda* produces a white precipitate in neutral solutions of protoxide of cerium.

A solution of *Oxalic Acid* produces, even in acid solutions of protoxide of cerium, if they do not contain too much free acid, an immediate white precipitate, which is soluble in a great excess of muriatic acid.

A solution of *Sulphate of Potash* produces in solutions of protoxide of cerium, when they are not too dilute, if not immediately, yet after some time, a crystalline precipitate, which is very sparingly soluble in water, and quite insoluble in a solution of sulphate of potash.

A solution of *Prussiate of Potash* produces a white precipitate in solutions of protoxide of cerium.

A solution of *Red Prussiate of Potash* produces no precipitate in solutions of protoxide of cerium.

Hydrosulphuret of Ammonia produces in neutral solutions of protoxide of cerium, a white precipitate of protoxide of cerium.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas,* produces no precipitate in solutions of protoxide of cerium.

The neutral solutions of protoxide of cerium redden litmus paper.

The salts of protoxide of cerium which dissolve in water, are decomposed by ignition; but the double sulphate of protoxide of cerium and potash forms an exception.

The detection of protoxide of cerium, in the compounds of protoxide of cerium which are insoluble in water, is attended with some difficulty. The best way to proceed is to dissolve such a compound in an acid, and to place a crust of crystals of sulphate of potash in the solution. This produces the double sulphate of protoxide of cerium

A solution of *Phosphate of Soda* produces in solutions of thorina, a white flocky precipitate, which is insoluble in an excess of phosphoric acid.

A solution of *Oxalic Acid* produces in solutions of thorina, a white, heavy precipitate, which is insoluble in an excess of oxalic acid and soluble in an extremely slight degree in other free and diluted acids.

A solution of *Sulphate of Potash* troubles the solutions of thorina very slowly, but if the solution of sulphate of potash be concentrated and added in excess, the whole of the thorina is finally precipitated, as a double salt.

A solution of *Prussiate of Potash* produces in neutral solutions of thorina, a white heavy precipitate, which is soluble in acids.

A solution of *Red Prussiate of Potash* produces no precipitate in solutions of thorina.

Hydrosulphuret of Ammonia produces in neutral solutions of thorina, a precipitate of hydrate of thorina.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces no precipitate in solutions of thorina.

The salts of thorina which dissolve in water, are decomposed by ignition.—The solutions of many of its salts are precipitated by boiling; for example, the solution of the sulphate is thus acted upon. This reaction does not take place, however, when bases are present with which thorina produces double salts.

Solutions of thorina are distinguished from solutions of alcalies, as well as from those of barytes, strontian, and lime, by giving a precipitate with ammonia; from solutions of magnesia, by its behaviour towards ammonia and hydrosulphuret of ammonia; and from solutions of alumina and glucina, by producing with a solution of potash, a precipitate which does not redissolve in an excess of the precipitant.

XII. YTTRIA.

Pure hydrate of yttria has a white colour, which ignition renders dirty yellow. It easily dissolves in acids.

A solution of *Potash* produces in solutions of yttria, a white, voluminous precipitate, which is insoluble in an excess of the precipitant.

Ammonia behaves in the same manner.

A solution of *Carbonate of Potash* produces in solutions of yttria, a white voluminous precipitate, which is slightly soluble in a great excess of the precipitant.

A solution of *Bicarbonate of Potash* produces in solutions of yttria a white voluminous precipitate, which completely dissolves in a very great excess of the precipitant.

A solution of *Carbonate of Ammonia* behaves in the same manner.

A solution of *Phosphate of Soda* produces in solutions of the neutral salts of yttria, a white precipitate, which is soluble in muriatic acid, but can be again precipitated by boiling the acid solution.

A solution of *Oxalic Acid* produces even in slightly acid solutions of yttria a voluminous white precipitate, which dissolves in muriatic acid.

A solution of *Sulphate of Potash* produces a precipitate in solutions of yttria. The precipitate does not appear till after a considerable time, and is completely redissolved on the addition of water, even if the water contain sulphate of potash in solution.

A solution of *Prussiate of Potash* produces a white precipitate in solutions of yttria.

A solution of *Red Prussiate of Potash* produces no precipitate in solutions of yttria.

Hydrosulphuret of Ammonia produces in neutral solutions of yttria, a precipitate of yttria.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces no precipitate in solutions of yttria.

The solutions of the neutral salts of yttria redden litmus paper.

and potash, which is insoluble in a solution of sulphate of potash.

Before the *Blowpipe*, the protoxide of cerium is converted into the peroxide. This dissolves in borax and in microcosmic salt, producing in the outer flame a red bead, the colour of which diminishes, and often wholly disappears on cooling. In the inner flame, the bead loses all colour. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 88.)

Solutions of protoxide of cerium are distinguished from those of alcalies, barytes, strontian, lime and magnesia, in the same manner as solutions of alumina are distinguished from those substances. From alumina and glucina, the protoxide of yttrium is distinguished by its insolubility in an excess of potash; from thorina, by its relation to heat. The latter does not become red when ignited, neither does it give a coloured bead when fused with borax or microcosmic salt before the blowpipe. When this proof is made, the substance must of course have been freed from iron. Protoxide of cerium is distinguished from yttria in the same manner as from thorina, and also by its behaviour towards a solution of sulphate of potash.

A solution of protoxide of cerium which contains non-volatile organic substances, affords no precipitate with alcalies.

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b. PEROXIDE OF CERIUM.

Peroxide of cerium is brick-red and pulverulent. When heated with muriatic acid, it dissolves, under disengagement of chlorine gas. The solution then contains protochloride of cerium, and consequently behaves towards reagents precisely like the solutions of protoxide of cerium. Even when the peroxide is dissolved by boiling in diluted sulphuric acid, the solution behaves towards reagents like those of protoxide of cerium. Nevertheless, the white precipitates of protoxide of cerium have often in this case a tinge of yellow, attributable to an admixture of peroxide.

XIV. ZIRCONIA.

The hydrate of zirconia, like that of alumina, forms a pale-yellow, horny mass, which easily dissolves in acids (for example, muriatic acid), particularly when they are exposed to heat. When the hydrate of zirconia is ignited, it becomes incandescent at the moment of ignition. The zirconia produced by the ignition of the hydrate, has a white colour, and is insoluble in most acids. If, however, it be digested for a considerable time in sulphuric acid, it becomes soluble in boiling water.

The solution of zirconia in acids behaves towards reagents like the salts of zirconia which are soluble in water.

A solution of *Potash* produces in solutions of zirconia, as in solutions of alumina, a voluminous precipitate, which, in the present case, however, is insoluble in an excess of the precipitant.

Ammonia behaves in the same manner.

A solution of *Carbonate of Potash* produces in solutions of zirconia, a voluminous precipitate, which is slightly soluble in a great excess of the precipitant.

A solution of *Bicarbonate of Potash* behaves in the same manner.

A solution of *Carbonate of Ammonia* behaves in the same manner: yet an excess of the precipitant dissolves the precipitate with greater ease.

A solution of *Phosphate of Soda* produces a voluminous precipitate in solutions of zirconia.

A solution of *Oxalic Acid* produces in solutions of zirconia, a voluminous precipitate, which is soluble in a great excess of muriatic acid.

A concentrated solution of *Sulphate of Potash* produces in solutions of zirconia, after a short time, a white precipitate, which is soluble in a large quantity of muriatic acid. When this precipitate is produced in a warm solution, it is nearly insoluble both in water and acids.

and potash, which is insoluble in a solution of sulphate of potash.

Before the *Blowpipe*, the protoxide of cerium is converted into the peroxide. This dissolves in borax and in microcosmic salt, producing in the outer flame a red bead, the colour of which diminishes, and often wholly disappears on cooling. In the inner flame, the bead loses all colour. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 88.)

Solutions of protoxide of cerium are distinguished from those of alcalies, barytes, strontian, lime and magnesia, in the same manner as solutions of alumina are distinguished from those substances. From alumina and glucina, the protoxide of yttrium is distinguished by its insolubility in an excess of potash; from thorina, by its relation to heat. The latter does not become red when ignited, neither does it give a coloured bead when fused with borax or microcosmic salt before the blowpipe. When this proof is made, the substance must of course have been freed from iron. Protoxide of cerium is distinguished from yttria in the same manner as from thorina, and also by its behaviour towards a solution of sulphate of potash.

A solution of protoxide of cerium which contains non-volatile organic substances, affords no precipitate with alcalies.

b. PEROXIDE OF CERIUM.

Peroxide of cerium is brick-red and pulverulent. When heated with muriatic acid, it dissolves, under disengagement of chlorine gas. The solution then contains protochloride of cerium, and consequently behaves towards reagents precisely like the solutions of protoxide of cerium. Even when the peroxide is dissolved by boiling in diluted sulphuric acid, the solution behaves towards reagents like those of protoxide of cerium. Nevertheless, the white precipitates of protoxide of cerium have often in this case a tinge of yellow, attributable to an admixture of peroxide.

XIV. ZIRCONIA.

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The solution of zirconia in acids behaves towards reagents like the salts of zirconia which are soluble in water.

A solution of *Potash* produces in solutions of zirconia, as in solutions of alumina, a voluminous precipitate, which, in the present case, however, is insoluble in an excess of the precipitant.

Ammonia behaves in the same manner.

A solution of *Carbonate of Potash* produces in solutions of zirconia, a voluminous precipitate, which is slightly soluble in a great excess of the precipitant.

A solution of *Bicarbonate of Potash* behaves in the same manner.

A solution of *Carbonate of Ammonia* behaves in the same manner: yet an excess of the precipitant dissolves the precipitate with greater ease.

A solution of *Phosphate of Soda* produces a voluminous precipitate in solutions of zirconia.

A solution of *Oxalic Acid* produces in solutions of zirconia, a voluminous precipitate, which is soluble in a great excess of muriatic acid.

A concentrated solution of *Sulphate of Potash* produces in solutions of zirconia, after a short time, a white precipitate, which is soluble in a large quantity of muriatic acid. When this precipitate is produced in a warm solution, it is nearly insoluble both in water and acids.

A solution of *Prussiate of Potash* produces a white precipitate in solutions of zirconia.

A solution of *Red Prussiate of Potash* produces no precipitate in solutions of zirconia.

Hydrosulphuret of Ammonia produces in solutions of zirconia, a voluminous precipitate of zirconia.

Liquid Sulphuretted Hydrogen, and *Sulphuretted Hydrogen Gas*, produce no precipitate in solutions of zirconia.

The neutral solutions of zirconia redden litmus paper.

The salts of zirconia which are soluble in water, are decomposed by ignition.

The compounds of zirconia with acids, when insoluble in water, are, in many cases, difficult to be distinguished from pure zirconia.

Before the *Blowpipe*, zirconia cannot be distinctly distinguished from similar substances.

Solutions of zirconia are distinguished from solutions of alcalies, barytes, strontian, lime, and magnesia, in the same manner as solutions of alumina are distinguished from those substances. From alumina and glucina, zirconia is distinguished by its insolubility in an excess of potash. From thorina and yttria, by giving with a solution of sulphate of potash, when heated, a precipitate which is nearly insoluble, not only in water but in acids; while the precipitates produced by sulphate of potash in solutions of thorina and yttria, can be dissolved by a large quantity of water. Zirconia is also distinguished from yttria by being rendered insoluble in acids (with the exception of sulphuric acid) by ignition, whereas the ignited yttria dissolves pretty easily in muriatic acid. Finally, it is distinguished from protoxide of cerium by not acquiring the red colour of peroxide of cerium on exposure to heat, and by not producing when fused with borax or microcosmic salt before the blowpipe, a coloured bead, either before or after cooling, provided the zirconia has been completely freed from iron.

The presence of non-volatile organic substances in its solutions, hinders the precipitation of zirconia by alcalies.

XV. OXIDES OF MANGANESE.

a. PROTOXIDE OF MANGANESE.

In a pure state, this substance is pulverulent and of a greyish green colour. It is of rare occurrence in analytical examinations. It gradually becomes oxidised in the air, and turns brown. When it is free from deutoxide of manganese, it dissolves in muriatic acid, without disengagement of chlorine gas on exposure to heat.—The hydrate of the protoxide is white, but it very quickly becomes oxidised in the air, and changes to brown.

The solutions of the protoxide in acids behave towards reagents, like the salts of protoxide of manganese. These have generally a very pale red colour.

A solution of *Potash* produces in solutions of protosalts of manganese, a white precipitate, which, if air has access, very soon becomes yellowish, then brown, and finally black; this change of colour is particularly observable at the point, where the precipitate is in contact with the atmosphere. If to a solution of a protosalt of manganese, a solution of muriate of ammonia be added, and then a solution of potash, a white precipitate is likewise produced, which, however, does not become brown so soon, on being exposed to the influence of the atmosphere.

Ammonia produces in neutral solutions of the protosalts of manganese a white precipitate, which, if air has access, very soon turns brown, and finally, at the point of contact with the air, black. If a solution of muriate of ammonia has previously been added to the solution of manganese, ammonia brings forth no precipitate; and a solution of muriate of ammonia easily redissolves the precipitate which has been already formed in the solution of manganese by caustic ammonia. But the clear solution thus produced, if exposed to the atmosphere, becomes brown, and deposits the insoluble brownish black deutoxide of manganese. This happens first at the surface of the liquor, where the separated deutoxide fixes itself firmly on the sides of the vessel.—If the solution of manganese has been precipitated by caustic ammonia, and the whole has been so long a time exposed to the air that the precipitate has become brown, the addition of a solution of muriate of ammonia does not effect the solution of the whole precipitate, but merely dissolves that portion of protoxide which has not become more highly oxidised, and leaves undissolved the brownish black deutoxide produced by the oxidising action of the atmosphere.

A solution of *Carbonate of Potash* produces in solutions of protosalts of manganese a white precipitate, which on exposure to air, does not change its colour, but remains perfectly white. This precipitate is very slightly soluble in a solution of muriate of ammonia.

A solution of *Bicarbonate of Potash* produces in solutions of protosalts of manganese, a white precipitate. In diluted solutions the precipitate appears only after some time. If the solution of manganese contains muriate of ammonia, the addition of bicarbonate of potash does not produce an immediate precipitate; yet precipitation ensues after some time.

A solution of *Carbonate of Ammonia* produces in solutions of protosalts of manganese a white precipitate, which is not affected by the action of the air, and is very slightly soluble in a solution of muriate of ammonia.

A solution of *Phosphate of Soda* produces in solutions of protosalts of manganese a white precipitate, which remains unaltered when exposed to the atmosphere.

A solution of *Oxalic Acid,* added to concentrated neutral solutions of protosalts of manganese, produces, after some time, a white crystalline deposit of oxalate of manganese, which is insoluble in free oxalic acid. Even in concentrated solutions of protosulphate of manganese, the addition of a solution of oxalic acid produces crystalline oxalate of manganese. In diluted solutions of protosalts of manganese, these crystals of oxalate of manganese cannot be produced. They disappear upon the addition of sulphuric or muriatic acid.—Solutions of the *Oxalates* produce in solutions of protoxide of manganese, the same crystalline deposit of oxalate of manganese. When a solution of oxalic acid or of an oxalate has been added to a dilute solution of manganese, and no precipitate has been produced in consequence of the dilution, the addition of ammonia occasions the formation of a precipitate. If, however, the manganese solution contain muriate of ammonia, if it be acid, or if the quantity of oxalic acid or oxalate be too considerable, then the addition of ammonia effectuates no precipitation; but if air be then permitted to have access, the air effects the production of insoluble brownish black deutoxide of manganese.

A solution of *Prussiate of Potash* produces in solutions of protosalts of manganese a white or pale red precipitate, which is soluble in free acids.

A solution of *Red Prussiate of Potash* produces in solutions of protosalts of manganese a brown precipitate, which is not soluble in free acids.

Hydrosulphuret of Ammonia produces in neutral solutions of protosalts of manganese, a yellowish or flesh-red precipitate. The colour of the precipitate must, in small experiments, be judged of, when the precipitate has completely subsided, for the colour does not appear pure while the precipitate is suspended in the liquor, which receives a yellowish colour from the excess of the reagent. The precipitate does not redissolve in an excess of hydrosulphuret of ammonia. If the flesh-red precipitate of sulphuret of manganese come into contact with the air, if, for example, it be gathered upon a filter, it becomes oxidised at the surface, and assumes a brownish black colour.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas* produces in neutral solutions of protosalts of manganese, no precipitate, unless a very weak acid be combined with the manganese. But, after the addition of the liquid sulphuretted hydrogen, a pale flesh-red precipitate can be produced by adding a few drops of ammonia.

Of the protosalts of manganese which easily dissolve in water, none but the protosulphate of manganese can be ignited in contact with the air without being decomposed.

And even this salt, when it has been ignited too strongly, does not completely dissolve in water.

The solutions of the neutral protosalts of manganese are without action on litmus paper.

The compounds of protoxide of manganese with acids, which, in a neutral state, are insoluble in water, can be dissolved by free acids, for instance, by diluted sulphuric or muriatic acid. To detect the presence of protoxide of manganese in these solutions, the operator first neutralises the free acid by ammonia, and then adds hydrosulphuret of ammonia. This occasions the precipitation of sulphuret of manganese, the yellowish or flesh-red colour of which is very characteristic. The protosalts of manganese which are insoluble in water, are commonly precipitated by ammonia with the peculiar white colour of manganese; but this is converted by the hydrosulphuret of ammonia into flesh red. When the protoxide of manganese is combined with an acid which is, in a free state, precipitable by hydrosulphuret of ammonia, such as arsenic acid, which produces sulphuret of arsenic, it is then necessary to add an excess of hydrosulphuret of ammonia. This redissolves the metallic sulphuret produced by the radical of the acid, but leaves the sulphuret of manganese undissolved.

The protosalts of manganese are extremely well characterised by their behaviour before the *Blowpipe*. When treated on charcoal with borax or microcosmic salt, they produce a bead which acquires in the outer blowpipe flame an amethyst colour, which disappears in the inner flame, and reappears in the outer. The smallest portion of manganese can be detected before the blowpipe, by fusing the salt with soda on platinum foil. The melted mass exhibits a green colour. (BERZELIUS: *Anwendung des Löthrohrs*, p. 89.)

Solutions of protosalts of manganese are so well characterised by their reaction with hydrosulphuret of ammonia, that they cannot be mistaken for solutions of alcaline or earthy salts.

When a solution of protoxide of manganese contains much organic matter, it is best to precipitate the manganese by hydrosulphuret of ammonia, and to examine the precipitated sulphuret of manganese before the blowpipe. When protoxide of manganese is contained in solid or pasty organic substances, the best way to proceed is to calcine a portion of the compound by the blowpipe flame on a piece of platinum foil, and to fuse the residue with soda on the same support.

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b. DEUTOXIDE OF MANGANESE.

Deutoxide of manganese in a pure state is black, and gives a black powder. It dissolves in muriatic acid, and produces a dark brown solution. This smells, even in the cold, of chlorine, because the perchloride of manganese is gradually reduced to protochloride. When the deutoxide is boiled with muriatic acid, this reduction is effected quickly. The solution then loses its dark colour, giving out at the same time, a strong smell of chlorine. The boiled solution behaves towards reagents like the solution of protoxide of manganese. If the deutoxide be digested with rather dilute sulphuric acid, it produces a violet-coloured solution, which is not so readily reduced by boiling as the muriatic acid solution. The decomposition of this solution is, however, effected easily by heating it with organic substances, such as sugar or alcohol; it is at the same time, deprived of its colour. The deutoxide of manganese scarcely dissolves in nitric acid.

The hydrate of deutoxide of manganese, which occurs native, is similar in appearance to the peroxide of manganese. In commerce, it is often mistaken for the latter substance, because when in a crystallised state, it has the same black colour. It is distinguished from the peroxide by giving a brown streak upon unglazed porcelain, while the streak given by the peroxide is black: it is farther distinguished from the peroxide of manganese by giving off water, when heated in a little glass tube closed at one end.

Before the *Blowpipe*, the deutoxide of manganese and its compounds, behave like the protoxide of manganése and the salts of the protoxide.

A solution of *Potash* produces in the muriatic acid solution of deutoxide of manganese a dark brown voluminous precipitate. The presence of muriate of ammonia does not hinder the production of this precipitate, nor yet of the precipitates described below.

Ammonia behaves in the same manner.

A solution of *Carbonate of Potash* produces in the muriatic acid solution of deutoxide of manganese, a brown voluminous precipitate.

A solution of *Bicarbonate of Potash* behaves in the same manner.

A solution of *Carbonate of Ammonia* has the same effect.

A solution of *Phosphate of Soda* produces in the muriatic acid solution of deutoxide of manganese, when the solution has been as accurately as possible neutralised by ammonia, a brown precipitate. This precipitate is far more voluminous and of a lighter colour than the precipitates produced by the reagents cited above.

A solution of *Oxalic Acid* produces no precipitate in the solution of deutoxide of manganese, but after some time, it renders the liquor colourless.

A solution of *Prussiate of Potash* produces in the solution of deutoxide of manganese, a greyish green precipitate.

A solution of *Red Prussiate of Potash* produces a brown precipitate, the same as in solutions of protoxide of manganese.

Hydrosulphuret of Ammonia produces in a solution of deutoxide of manganese which is saturated by ammonia, the same flesh-red precipitate as in solutions of protoxide of manganese. When a solution of deutoxide of manganese has been supersaturated by ammonia, and the deutoxide has been thereby thrown down as a dark brown precipitate, the addition of hydrosulphuret of ammonia converts the deutoxide into sulphuret, and changes its colour to flesh red.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas* produces in solutions of deutoxide of manganese, a milk-white precipitate of sulphur, while the deutoxide is reduced to protoxide.

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c. PEROXIDE OF MANGANESE.

The peroxide of manganese is black, and its crystals give a pure black streak upon unglazed porcelain. Ignition renders the peroxide of manganese brown; oxygen gas is disengaged, and the product is the intermediate oxide of manganese (Manganoxyd-oxydul); a pretty strong heat, however, is required to effect this change. When the peroxide is pure, it gives no water on being heated in a little glass tube closed at one end; if water is produced when the experiment is made, it proves that the peroxide contains hydrate of deutoxide, which is very frequently the case. In muriatic acid, the peroxide of manganese dissolves in the cold, and produces a brown solution containing deutoxide of manganese; chlorine gas is disengaged during the solution. In sulphuric acid, it dissolves at a boiling heat, under disengagement of oxygen gas. In this case, it produces a violet solution, which also contains deutoxide of manganese. The presence of organic substances promotes the solution of the peroxide. It is then, however, converted into protoxide, not under disengagement of chlorine or oxygen gas, but of carbonic acid gas.

XVI. OXIDE OF ZINC.

Oxide of zinc, in a pure state, is white. When heated, it assumes a lemon-yellow colour, but becomes white again as soon as it is cold.—It is not volatilized by heat. It dissolves readily in acids, even after having been strongly heated. The solution behaves towards reagents like the solutions of salts of oxide of zinc.

A solution of *Potash* produces, in solutions of zinc salts, a white gelatinous precipitate, which redissolves in an excess of the precipitant.

Ammonia behaves in the same manner.

A solution of *Carbonate of Potash* produces, in solutions of zinc, a white precipitate, which is soluble in no excess of the precipitant; it dissolves, however, in a solution of potash or ammonia. If the solution contain muriate of ammonia, carbonate of potash produces no precipitate in the cold; but, if the solution be boiled until the ammoniacal salt is decomposed, then a precipitate is formed.

A solution of *Bicarbonate of Potash* produces a white precipitate, under disengagement of carbonic acid gas.

A solution of *Carbonate of Ammonia* produces a white precipitate, which dissolves in an excess of the precipitant.

A solution of *Phosphate of Soda* gives, with neutral zinc solutions, a white precipitate, which is soluble in acids, in potash, and in ammonia.

A solution of *Oxalic Acid* produces, in neutral zinc solutions, a white precipitate, which, on reposure, becomes more considerable. In very dilute solutions, this reagent produces no immediate precipitate, though a troubling is visible after some time. Precipitation is also effected by a solution of *Binoxalate of Potash*. The precipitate produced by oxalic acid in zinc solutions, is soluble in potash and ammonia, and in muriatic and other acids. The presence of muriate of ammonia does not hinder the precipitation by oxalic acid.

A solution of *Prussiate of Potash* produces, in zinc solutions, a white gelatinous precipitate, which is insoluble in free muriatic acid.

A solution of *Red Prussiate of Potash* produces, in solutions of zinc, a yellowish-red precipitate, which is soluble in free muriatic acid.

Hydrosulphuret of Ammonia produces, in neutral solutions of zinc, a white precipitate of sulphuret of zinc, which is insoluble in an excess of the precipitant. If the solution contain the least trace of iron, the colour of the precipitate is grey. If a large quantity of iron be present, the precipitate is black.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas* produces, in neutral zinc solutions, a white precipitate of sulphuret of zinc; but it produces no precipitate in acidulated solutions.

All the zinc salts which are soluble in water are decomposed when heated to redness in contact with the air, and are afterwards insoluble in water. The sulphate of zinc, however, is only partially decomposed, even when ignited very strongly.

The solutions of the neutral zinc salts redden litmus paper.

The salts of zinc which are insoluble in water, dissolve in free acids, for example, in diluted sulphuric or muriatic acid. When the acid solution is saturated by ammonia or potash, the insoluble zinc compound is precipitated, yet it generally redissolves in an excess of the precipitant. From an alcaline solution of this description, hydrosulphuret of ammonia precipitates the whole of the oxide of zinc in the state of white sulphuret of zinc. This is the most certain method of detecting the presence of zinc in compounds which are insoluble in water; for, a white precipitate, produced in a clear and strongly alcaline solution by hydrosulphuret of ammonia, can consist of nothing else than sulphuret of zinc.

Before the *Blowpipe*, the zinc salts are peculiarly easy of detection. If heated on charcoal, with soda, in the interior flame, they spread on the charcoal a white coat of oxide of zinc. Moistened with nitrate of cobalt, and heated in the blowpipe flame, they assume a fine green colour. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 91.)

Salts of oxide of zinc in solution, are distinguished from solutions of alcaline salts by their behaviour with carbonate of potash. They are distinguished from solutions of earthy salts by giving a white precipitate when tested with hydrosulphuret of ammonia, and that even when they have previously been dissolved by potash or ammonia. This effect does not take place even with the solutions of aluminous salts in potash.

When a solution of oxide of zinc contains a large quantity of non-volatile organic substances, the operator supersaturates the solution with ammonia, and separates the precipitate, when there is any, by filtration. He then tests the solution with hydrosulphuret of ammonia. This precipitates the oxide of zinc, in the state of sulphuret, which must be farther examined, particularly when it is not of a white colour, but tinged grey or black by sulphuret of iron, before the blowpipe. The presence of a small quantity of oxide of zinc in solid or pasty organic substances, is often very difficult of detection. The substances which are suspected to contain it, must be digested with diluted nitric acid. The filtered solution must then be treated with ammonia and hydrosulphuret of ammonia, in the manner which has been just described. The organic substance can also be previously charred, but care must be taken to employ only a gentle heat, lest the oxide of zinc be reduced, and the metallic zinc be volatilized. The charred mass is then digested with nitric acid, and the resulting solution is treated in the manner described above.

XVII. OXIDES OF COBALT.

a. OXIDE OF COBALT.

In a pure state, this oxide has a greenish-grey colour. Its hydrate, in a dry state, is reddish. It dissolves in acids. As it frequently contains peroxide, it very often disengages chlorine, on being dissolved in muriatic acid.

A solution of *Potash* produces, in solutions of cobalt, a blue precipitate, which turns green when allowed to repose, and dirty pale red when boiled. The precipitate also acquires this pale red colour without being heated, when it is suffered to remain a long time at the bottom of the solution. When the precipitate is gathered upon a filter, the blue colour is soon replaced by green. An excess of the solution of potash does not redissolve it.

Ammonia produces, in cobalt solutions, a blue precipitate; a larger quantity of ammonia renders the precipitate green, and when still more ammonia is added, the precipitate mostly dissolves, forming a green solution, and leaving only a very small green precipitate. This solution changes its colour on exposure to the air; the change commencing at the surface. It continually becomes darker, and finally appears of a dark brown colour. If the cobalt solution contains muriate of ammonia, the addition of caustic ammonia produces no precipitate; the solution remains red, but after some time becomes brown, the change of colour commencing at the surface. A solution of potash produces no precipitate in such an ammoniacal solution of oxide of cobalt, provided it contain muriate of ammonia; but if the solution contain no muriate of ammonia, it produces a very slight precipitate.

A solution of *Carbonate of Potash* produces, in cobalt solutions, a red precipitate, which, upon being boiled, becomes blue.

A solution of *Bicarbonate of Potash* produces, in cobalt solutions, a red precipitate.

A solution of *Carbonate of Ammonia* produces, in neutral cobalt solutions, a red precipitate, which dissolves in a solution of muriate of ammonia. The solution thus formed has a red colour, and does not turn brown on exposure to the air, but merely becomes a very little redder at the surface, and that only after a pretty long exposure. When the solution of oxide of cobalt contains muriate of ammonia, the addition of carbonate of ammonia produces no precipitate.

A solution of *Phosphate of Soda* produces, in neutral cobalt solutions, a blue precipitate.

A solution of *Oxalic Acid* produces, in neutral cobalt solutions, no immediate troubling; but, after some time, there appears a precipitate, which is white or only very slightly reddish. This precipitate continually increases in quantity during a long reposure, so that at last the supernatant solution becomes nearly colourless.

A solution of *Prussiate of Potash* produces, in cobalt solutions, a green precipitate, which afterwards turns grey, and is insoluble in muriatic acid.

A solution of *Red Prussiate of Potash* produces, in cobalt solutions, a dark reddish-brown precipitate, which is insoluble in muriatic acid.

Hydrosulphuret of Ammonia produces, in neutral cobalt solutions, a black precipitate, which is insoluble in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, causes, in neutral cobalt solutions, no immediate precipitation; the solution, however, acquires a somewhat blackish colour, and after some time deposits a very slight black precipitate. An acidulated solution affords not the slightest signs of a precipitate, even after a considerable time.

All the salts of oxide of cobalt which are soluble in water, are decomposed when heated to redness in contact with the atmosphere, and become thereon partially insoluble in water. The sulphate of cobalt, however, is but partially decomposed, even by a very strong heat.

The solutions of the neutral cobalt salts weakly redden litmus paper.

The salts of oxide of cobalt which are insoluble in water, nearly all dissolve in acids, for example, in muriatic or sulphuric acid. When the solution produced by dissolving such a compound in an acid, is saturated by potash, or still better by ammonia, the insoluble compound commonly precipitates in its original state. When, however, the solution is very acid, the saturation of it with ammonia produces no precipitate; because, in that case, the precipitation is hindered by the presence of the ammoniacal salt. Hydrosulphuret of ammonia, however, produces immediately a black precipitate, and it is by means of this reagent that the analyst can most easily convince himself of the presence of cobalt in a solution. Whenever no precipitate is produced in the acidulated solution of a compound by sulphuretted hydrogen gas, while, at the same time, a black precipitate is produced in the neutral or alcaline solution by hydrosulphuret of ammonia, the substance can scarcely contain any other metal than cobalt, nickel, or iron. The method of distinguishing these three metals from each other, is described in another part of this work.

Before the *Blowpipe*, the cobalt salts are very easily detected. The smallest portions colour borax and microcosmic salts strongly blue; by larger quantities, the glass is so fully coloured, that it appears to be black. By soda, on charcoal, they are reduced to a grey magnetic powder, which is metallic cobalt. (BERZELIUS: *Anwendung des Löthrohrs*, p. 93.)

The solutions of the salts of oxide of cobalt are peculiarly distinguished from those of all the salts which have been hitherto spoken of, by the black precipitate which they produce with hydrosulphuret of ammonia. In the solid state, they are easily distinguished from other substances by their behaviour before the blowpipe.

Many non-volatile organic substances hinder the precipitation of oxide of cobalt by alcalies, but not the precipitation by hydrosulphuret of ammonia.

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b. PEROXIDE OF COBALT.

This has a black colour. It disengages oxygen gas when strongly heated. Concentrated and boiling muriatic acid dissolves it, under disengagement of chlorine gas. Before the blowpipe, it behaves like oxide of cobalt.

XVIII. OXIDES OF NICKEL.

a. OXIDE OF NICKEL.

The pure oxide is dark grey; the hydrate is green. It dissolves in acids. The solution has a green colour, and behaves towards reagents like the solutions of the salts of oxide of nickel which are soluble in water.

A solution of *Potash* produces, in solutions of oxide of nickel, an apple-green precipitate, which an excess of potash does not redissolve.

Ammonia, added in extremely small proportion to nickel solutions, produces a very inconsiderable green troubling, which, upon the addition of a larger quantity of ammonia, very speedily disappears. The clear solution thus formed,

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has a fine blue colour, with a slight tendency to violet. A solution of potash produces, in this ammoniacal solution, an apple-green precipitate.

A solution of *Carbonate of Potash* produces, in nickel solutions, an apple-green precipitate, which has a lighter colour than the precipitate produced in nickel solutions by potash.

A solution of *Bicarbonate of Potash* likewise produces, in nickel solutions, a light apple-green precipitate, and disengages a portion of carbonic acid gas.

A solution of *Carbonate of Ammonia* produces, in neutral solutions of nickel, an apple-green precipitate, which redissolves in an excess of the carbonate of ammonia, and forms a bluish-green solution.

A solution of *Phosphate of Soda* produces, in neutral nickel solutions, a white precipitate, slightly tending to green.

A solution of *Oxalic Acid* produces, in neutral solutions of nickel, no immediate precipitate. After some time, however, a greenish precipitate appears, which is very much increased after a long reposure, so that the solution above it becomes nearly colourless.

A solution of *Prussiate of Potash* produces, in nickel solutions, a white precipitate, slightly tending to green. It is insoluble in muriatic acid.

A solution of *Red Prussiate of Potash* gives, with nickel solutions, a yellowish-green precipitate, which is insoluble in muriatic acid.

Hydrosulphuret of Ammonia produces, in neutral nickel solutions, a black precipitate, and communicates, at the same time, a black colour to the supernatant fluid. The precipitate is nearly insoluble in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas* produces, in neutral nickel solutions, no immediate precipitate. The solution becomes somewhat blackish, and after a long time, a very small black precipitate appears. No precipitate is produced in an acidulated solution, even after a long reposure.

All the salts of oxide of nickel which are soluble in water, are decomposed when heated to redness in contact with the air, and subsequently do not completely dissolve in water. Nevertheless, the sulphate of nickel is only partially decomposed, even by a very strong heat.

The solutions of the neutral nickel salts slightly redden litmus paper.

The salts of oxide of nickel which are insoluble in water, nearly all dissolve in acids, for example, in muriatic or diluted sulphuric acid. If such a solution is supersaturated with ammonia, the salt is not precipitated. If, however, the solution be not too dilute, it acquires a blue colour, and thus indicates the presence of oxide of nickel.

Before the *Blowpipe*, the nickel salts can be detected by fusing a portion with borax or microcosmic salt in the outer flame; they communicate to the bead a reddish colour, the intensity of which diminishes as the bead cools, and often quite disappears when it is completely cold. With soda or charcoal, they are reduced to a white metallic magnetic powder. (BERZELIUS : *Ueber die Anwendung des Löthrohrs*, p. 94.)

The solutions of the salts of oxide of nickel are distinguished from those of all the salts which have hitherto been spoken of, those of oxide of cobalt excepted, by their behaviour with hydrosulphuret of ammonia. They are distinguished from oxide of cobalt solutions by their behaviour with ammonia, and by the behaviour of the ammoniacal solution with potash.

A great number of non-volatile organic substances hinder the precipitation of oxide of nickel by alcalies, but not by hydrosulphuret of ammonia.

b. PEROXIDE OF NICKEL.

This has a black colour. When ignited, it disengages oxygen gas. It is dissolved by concentrated muriatic acid, under disengagement of chlorine gas. Before the blowpipe, it behaves like oxide of nickel.

XIX. OXIDES OF IRON.

a. PROTOXIDE OF IRON.

This oxide in a pure state, is nearly unknown. Even its hydrate has never been produced in a state of dryness and purity. The reason of this is, that when precipitated from a solution, it becomes with great ease more highly oxidised in the air, particularly at the surface. It is, however, not only contained in solutions of the protosalts of iron, but is produced whenever iron is dissolved in diluted sulphuric or muriatic acid.

A solution of *Potash* produces in solutions of protoxide of iron, a flocky precipitate. This is nearly white at first, but after a very short time, becomes grey and then green; at the point, where it is in contact with atmospheric air, it becomes still darker and finally reddish brown. If the solution is filtered while the precipitate is green, the latter, by being gathered upon the filter, is very much exposed to the air, and soon becomes reddish brown.

Ammonia produces with solutions of protoxide of iron the same appearances as potash. If a solution of muriate of ammonia has been previously mingled with the iron solution, the addition of ammonia produces no precipitate; yet when the mixture is exposed to the air, there is soon formed a small quantity of a green precipitate which becomes reddish brown at the surface.

A solution of *Carbonate of Potash* produces in solutions of protoxide of iron, a white precipitate, without the occurrence of effervescence from the discharge of carbonic acid gas. This precipitate of carbonate of iron does not so soon become green and reddish brown at the surface as the precipitate formed by solutions of pure potash. It dissolves in a solution of muriate of ammonia; yet when the solution is placed in contact with the air, a green precipitate is formed, which at the surface of the liquid becomes reddish brown. But this precipitate appears later than it would have done had ammonia, instead of carbonate of potash, been added to the liquid.

A solution of *Bicarbonate of Potash* produces in solutions of protoxide of iron, under disengagement of carbonic acid gas, a white precipitate of carbonate of iron.

A solution of *Carbonate of Ammonia* behaves with solutions of protoxide of iron, the same as a solution of carbonate of potash.

A solution of *Phosphate of Soda* produces in neutral solutions of protoxide of iron a white precipitate, which, on being exposed to the air for some time, becomes green.

Solutions of *Oxalic Acid* and *Binoxalate of Potash,* when added to solutions of protoxide of iron, immediately communicate a yellow colour to them, and after some time produce a yellow precipitate of protoxalate of iron. This precipitate dissolves in an excess of muriatic acid. Neutral alcaline oxalates produce the same precipitate immediately, and still more distinctly.

A solution of *Prussiate of Potash* produces in solutions of protoxide of iron a precipitate, which, if air be completely excluded is, at the instant of its production, white, but otherwise always appears of a light blue colour. Upon longer exposure to the air, it becomes dark blue. It is insoluble in muriatic acid.

A solution of *Red Prussiate of Potash* produces in solutions of protoxide of iron, an immediate dark blue precipitate, which is insoluble in acids.

Hydrosulphuret of Ammonia produces in neutral solutions of protoxide of iron, a black precipitate of sulphuret of iron, which becomes oxidised when placed in contact with the air, and turns reddish brown. This character serves to distinguish sulphuret of iron from the sulphurets of nickel and cobalt. The precipitated sulphuret of iron is insoluble in an excess of hydrosulphuret of ammonia.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas,* produces in neutral solutions of protoxide of iron, no precipitate.

The protosalts of iron which are soluble in water are decomposed when ignited in contact with the air.

The solutions of the neutral protosalts of iron redden litmus paper.

The salts of protoxide of iron which are insoluble in water, are nearly all soluble in muriatic acid or diluted sulphuric acid. When the resulting acid solution is supersaturated with ammonia, the insoluble salt generally precipitates. If, however, hydrosulphuret of ammonia be added, the precipitated salt immediately acquires a black colour.

Before the *Blowpipe*, the protosalts of iron can be very easily detected by fusing a portion on charcoal with borax or microcosmic salt;—in the outer flame the glass acquires a deep red colour, which becomes lighter on cooling; in the inner flame, the colour produced is green, which totally disappears when the glass is cold, if the iron be not present in too large a quantity. The smallest quantities of protoxide of iron can be detected by fusing the substance in microcosmic salt, which is coloured green thereby, even when heated in the outer flame; the colour decreases in intensity while the glass is cooling, and totally disappears when it is quite cold. When fused with soda on charcoal, the protosalts of iron are reduced, and give, after the grinding and separating of the charcoal, a magnetic, metallic powder. (BERZELIUS: *Anwendung des Löthrohrs*, p. 92.)

The solutions of protoxide of iron can readily be discriminated by their behaviour with hydrosulphuret of ammonia and with the red prussiate of potash.

The presence of a large quantity of non-volatile organic substances, hinders the precipitation of protoxide of iron by alcalies.

b. PEROXIDE OF IRON.

In a state of purity, the peroxide of iron, when in powder, possesses a reddish brown colour. That which occurs native in a crystallised state (iron glance) is of a grey colour and exhibits the metallic lustre. The peroxide of iron, when precipitated from its solution and exposed to ignition, becomes black. Yet both the black substance and the iron glance, afford a red powder. The recently precipitated peroxide is easily soluble in acids. The solution is effected with much more difficulty when the peroxide has been ignited. The ignited peroxide is nevertheless completely soluble, and with most ease in muriatic acid.

A solution of *Potash* produces in solutions of peroxide of iron, a reddish brown voluminous precipitate, which is insoluble in an excess of the precipitant.

Ammonia behaves with solutions of peroxide of iron, in the same manner as potash.

A solution of *Carbonate of Potash* precipitates solutions of peroxide of iron also with a reddish brown colour; but the colour of the precipitate is somewhat lighter than the colour of those produced by pure potash and ammonia.

A solution of *Bicarbonate of Potash* produces, under disengagement of carbonic acid gas, a light reddish brown precipitate. Through boiling, during which more carbonic acid gas escapes, the precipitate acquires a darker colour.

A solution of *Carbonate of Ammonia* behaves with solutions of peroxide of iron like a solution of carbonate of potash.

A solution of *Phosphate of Soda* forms in neutral solutions of persalts of iron, a white precipitate. Upon the addition of ammonia, this precipitate becomes brown, and after some time completely dissolves.

A solution of *Oxalic Acid* gives with neutral solutions of peroxide of iron, no precipitate; but the solution acquires a yellowish colour.

A solution of *Prussiate of Potash* produces in solutions of peroxide of iron, an immediate dark blue precipitate, which is insoluble in muriatic acid.

A solution of *Red Prussiate of Potash* produces in solutions of peroxide of iron, no precipitate; but the solution often becomes somewhat darker coloured.

Hydrosulphuret of Ammonia produces in neutral solutions of peroxide of iron, a black precipitate, which is insoluble in an excess of the precipitant. If left in contact with atmospheric air, it becomes oxidised and obtains a reddish brown colour.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces in neutral solutions of peroxide of iron, a milky-white precipitate of separated sulphur. The solution then contains protoxide of iron.

None of the persalts of iron which are soluble in water can be heated to redness in contact with the air without undergoing decomposition.

The solutions of the neutral persalts of iron redden litmus paper.

The salts of peroxide of iron which are insoluble in water, dissolve in muriatic acid or in diluted sulphuric acid. If a solution of potash or ammonia be added to the resulting acid solution, and that in quantity but little beyond what is requisite to saturate the acid, the insoluble compound is generally precipitated in an undecomposed state, and possessed of its characteristic colour, which, for example, in the case of the phosphate and arseniate of peroxide of iron, is white. But the greater the quantity of these alcalies, and particularly of potash, which may be added, so much the more has the precipitate a tendency to exhibit a reddish brown colour. Hydrosulphuret of ammonia instantly renders these precipitates black.

Before the *Blowpipe*, the persalts of iron behave precisely like the protosalts of iron.

Solutions of the peroxide of iron are easily recognised by their behaviour with liquid sulphuretted hydrogen, with hydrosulphuret of ammonia, and with a solution of prussiate of potash; and are thus distinguished from solutions of other bases.

All non-volatile organic substances completely hinder the precipitation of peroxide of iron by alcalies, unless they be present in but very small proportion. They do not however hinder the production of a precipitate by a solution of prussiate of potash. If a solution containing peroxide of iron in a state of mixture with organic matter, remain clear after being supersaturated with ammonia, it affords a black precipitate of sulphuret of iron, on being tested by hydrosulphuret of ammonia.

COMPOUNDS of PROTOXIDE OF IRON with PEROXIDE OF IRON occur very frequently in a native state. Mineralogists call them magnetic iron ore. They are also produced when iron is ignited in the open air (Hammerschlag). These compounds are black. To detect therein the presence of both oxides, the operator dissolves the compound in a closed flask in concentrated muriatic acid. He adds to one portion of this solution, a saturated solution of sulphuretted hydrogen. The milky white precipitate of separated sulphur which is thus produced, indicates the presence of peroxide of iron. Another portion of the solution is diluted with water, and tested by a solution of red prussiate of potash. The resulting dark blue precipitate indicates the presence of protoxide of iron.

XX. OXIDE OF CADMIUM.

Pure oxide of cadmium has a reddish brown colour, or at least it gives a reddish brown powder. It is not volatilized by heat; but when it is mingled with organic substances or with charcoal powder, it is then volatilized upon being heated. The reason of this is, that the oxide is then reduced to metallic cadmium, which is very volatile.—The hydrate of oxide of cadmium is white. When heated, it loses its water, and acquires the reddish brown colour of the oxide.

It easily dissolves in acids. The solution behaves towards reagents precisely like the solutions of the soluble salts of oxide of cadmium.

A solution of *Potash* produces in solutions of oxide of cadmium, a white precipitate, which is insoluble in an excess of potash.

Ammonia produces in neutral cadmium solutions, a white precipitate, which very easily dissolves in a slight excess of ammonia.

A solution of *Carbonate of Potash* produces in cadmium solutions, a white precipitate, which is insoluble in an excess of carbonate of potash.

A solution of *Bicarbonate of Potash* likewise produces in neutral cadmium solutions, and under disengagement of carbonic acid gas, a white precipitate.

A solution of *Carbonate of Ammonia* produces in solutions of cadmium, even when they contain much muriate of ammonia, a white precipitate, which is insoluble in an excess of the carbonate of ammonia.

A solution of *Phosphate of Soda* produces a white precipitate in neutral solutions of cadmium.

A solution of *Oxalic Acid* immediately produces a precipitate in neutral solutions of cadmium. The precipitate is easily soluble in pure ammonia.

A solution of *Prussiate of Potash* produces in cadmium solutions, a white precipitate, passing a very little into yellowish. This precipitate is soluble in muriatic acid.

A solution of *Red Prussiate of Potash* produces in cadmium solutions, a yellow precipitate, which is soluble in muriatic acid.

Hydrosulphuret of Ammonia produces in neutral cadmium solutions, a yellowish precipitate, which is insoluble in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces either in neutral or acidulated cadmium solutions, a yellow precipitate.

A bar of *Metallic Zinc* precipitates cadmium from its solutions in the metallic state, and in the form of small glancing grey-coloured spangles.

The salts of oxide of cadmium which are soluble in water, cannot be heated to redness in contact with the air without experiencing decomposition.

The solutions of the neutral cadmium salts redden litmus paper.

The salts of oxide of cadmium which are insoluble in water, dissolve in acids. The presence of oxide of cadmium is very easily detected in these acid solutions by the yellow precipitate produced by liquid sulphuretted hydrogen, or a current of sulphuretted hydrogen gas.

Before the *Blowpipe*, the cadmium salts can be detected by mingling a portion with soda, and heating it on charcoal in the inner flame; upon which, the charcoal is bedecked with a brownish red powder. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 91.)

The solutions of oxide of cadmium can be easily recognised from their behaviour with liquid sulphuretted hydrogen, and hydrosulphuret of ammonia. They are distinguished by these reagents from solutions of all the bases hitherto treated of.

The presence of non-volatile organic substances hinders the precipitation of oxide of cadmium by pure potash, but does not influence the action of the alcaline carbonates.

XXI. OXIDES OF LEAD.

a. PROTOXIDE OF LEAD.

Pure protoxide of lead is yellow, but its powder has a reddish hue. It easily melts at a red heat, and when it has been melted in considerable quantity is scaly, and of a yellowish red or a yellow colour, but its powder is reddish yellow. At a white heat it volatilizes, particularly if air be present. When protoxide of lead is mingled with organic substances, or with charcoal powder, it is very easily reduced by heat. It is not quite insoluble in water. The best solvent of protoxide of lead is nitric acid, or acetic acid. When it does not wholly dissolve in these acids, it is impure. The litharge which is found in commerce, very often contains silica, and this remains undissolved when the litharge is treated with acids. The solution behaves towards reagents like the aqueous solutions of the salts of protoxide of lead.

A solution of *Potash* produces in solutions of protoxide of lead a white precipitate, which redissolves in a considerable excess of the precipitant.

Ammonia produces a white precipitate, which is not soluble in an excess of ammonia. (A solution of acetate of lead, even when much concentrated, is not troubled by ammonia: but after some time a sub-salt is deposited.)

A solution of *Carbonate of Potash* produces, in solutions of protoxide of lead, a white precipitate, which is insoluble in an excess of the carbonate of potash, but soluble in pure potash.

A solution of *Bicarbonate of Potash* produces, under disengagement of carbonic acid gas, a similar precipitate.

A solution of *Carbonate of Ammonia* behaves with solutions of protoxide of lead like a solution of carbonate of potash.

A solution of *Phosphate of Soda* forms in neutral solutions of lead a white precipitate, which is soluble in a solution of pure potash.

A solution of *Oxalic Acid* produces in neutral solutions of protoxide of lead an immediate white precipitate.

A solution of *Prussiate of Potash* produces in solutions of protoxide of lead, a white precipitate.

A solution of *Red Prussiate of Potash* produces no precipitate in solutions of protoxide of lead.

Hydrosulphuret of Ammonia produces in solutions of protoxide of lead, a black precipitate, which is insoluble in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces in neutral and acid solutions of protoxide of lead, a black precipitate.

A bar of *Metallic Zinc* precipitates lead from its solutions in the metallic state, and in the form of blackish-grey shining spangles.

The solutions of protoxide of lead are also precipitated by several reagents, which produce no precipitates in solutions of most of the oxides which have hitherto been treated of.

Diluted *Sulphuric Acid* and solutions of the *Sulphates* produce in solutions of protoxide of lead, a white precipitate, which is insoluble or sparingly soluble in diluted acids, but soluble in a solution of potash. The production of this precipitate is an excellent method of determining the presence of protoxide of lead; because sulphuric acid produces precipitates which are characterised by insolubility in diluted acids, with no other substances than alcaline earths and protoxide of lead. Sulphate of lead is distinguished from the earthy sulphates by being soluble in a solution of potash, and more particularly by instantly assuming a black colour on being moistened with hydrosulphuret of ammonia.

Muriatic Acid and solutions of *Chlorides* produce in solutions of protoxide of lead, when they are not very dilute, a white precipitate, which redissolves, however, on the addition of water. In this solution of chloride of lead, ammonia produces a white precipitate. The precipitate produced by muriatic acid, or by solutions of chlorides, in solutions of protoxide of lead, is also soluble in potash.

A solution of *Iodide of Potassium* produces in solutions of protoxide of lead, a yellow precipitate, which is soluble in a great excess of the precipitant.

A solution of *Chromate of Potash* produces in solutions of protoxide of lead, a yellow precipitate, which is insoluble in diluted nitric acid, but soluble in a solution of pure potash.

The salts of protoxide of lead which are soluble in water cannot be heated to redness, in contact with the air, without suffering decomposition.

The solutions of the neutral salts of protoxide of lead redden litmus paper.

Most of the salts of protoxide of lead which are insoluble in water, dissolve in nitric acid. The resulting acid solution, after being diluted with water, and if the solution be not too acid, affords a precipitate with sulphuric acid. The sulphate of lead is insoluble in diluted nitric acid. It is nevertheless easy to recognise it for a metallic salt, for it becomes instantly black on being moistened with hydrosulphuret of ammonia, and when treated with soda on charcoal before the blowpipe, very easily affords metallic lead.

Before the *Blowpipe*, the salts of protoxide of lead can be readily recognised by being mingled with soda and heated on charcoal, in the inner flame; upon which they are reduced to metallic globules, which can easily be flattened by the hammer, and are not brittle. During the operation, the charcoal receives a coating of yellow powder. (BERZELIUS: *Anwendung des Löthrohrs*, p. 98.)

The solutions of protoxide of lead can be easily distinguished from the solutions of other oxides, by their behaviour towards diluted sulphuric acid. From the solutions of the alcaline earths, they are distinguished by their reaction with hydrosulphuret of ammonia.

When a solution of protoxide of lead contains a very great quantity of organic substances, so as even to be very strongly coloured thereby, it still affords a precipitate with sulphuric acid. The presence of lead can be very easily detected in the precipitated sulphate, by fusing it with soda on charcoal before the blowpipe. If the solution contain gum, the sulphate of lead does not readily subside, but remains for a long time suspended in the liquid, and is filtered with difficulty.

If a solution which contains much organic matter, contain merely traces of protoxide of lead, then no precipitate is produced by sulphuric acid. In this case, the solution must be slightly acidulated by nitric acid, and be subjected to a current of sulphuretted hydrogen gas. The protoxide of lead is thus completely precipitated in the state of sulphuret of lead. The precipitate does not fully subside, however, till after some time. When the solution is of small bulk, the lead can be sufficiently well precipitated, in the state of sulphuret, by merely adding an excess of liquid sulphuretted hydrogen. The precipitate must in this case also, be fused with soda on charcoal before the blowpipe, for the purpose of demonstrating the presence of lead.—When protoxide of lead is mingled with solid or pasty organic substances, it is best to mix the whole with carbonate of soda, and to ignite it in a covered

Hessian crucible; but the operator must take care not to employ too powerful a heat in this operation, lest the reduced lead be volatilized. After becoming cool, the fused mass is pulverised in an agate mortar with water, and the charcoal is carefully washed away. The reduced metallic lead then remains behind in the mortar, and can easily be recognised.

b. RED OXIDE OF LEAD *(Minium)*.

This oxide is pulverulent, and has a brick-red colour. When gently heated, it turns black, but again becomes red on cooling. By a strong heat, it is converted into protoxide of lead, under disengagement of oxygen gas. If red oxide of lead be adulterated, as it sometimes is, with brick-dust, the latter is best detected by treating the ignited oxide with diluted nitric acid; the brick-dust then remains undissolved. When the red oxide of lead is put into nitric or acetic acid, it becomes brown; the reason of this alteration is, that the red oxide is converted, partly into protoxide which dissolves in the acid, and partly into brown oxide which remains undissolved. When the red oxide is heated with muriatic acid, chlorine gas is disengaged, and chloride of lead produced.

Before the *Blowpipe*, the red oxide of lead behaves like the protoxide, into which, indeed, it is converted by heat.

c. BROWN OXIDE OF LEAD.

This oxide is dark brown, and pulverulent. When heated, it gives out oxygen gas, and is converted into protoxide of lead, without being previously converted into red oxide. When treated with muriatic acid, it is converted, even in the cold, into chloride of lead; the conversion being accompanied by the disengagement of gaseous chlorine.

Before the *Blowpipe*, it behaves like protoxide of lead.

XXII. OXIDE OF BISMUTH.

Pure oxide of bismuth is yellow. It becomes darker when heated, but upon cooling regains its original colour. In a strong heat, it fuses to a yellow glass. It does not volatilise, except at an extremely high temperature. It is very easily reduced to metallic bismuth by ignition with organic substances or charcoal powder. The oxide of bismuth readily dissolves in acids.

A great number of salts of oxide of bismuth dissolve in water, but the solution is not complete. The salt is decomposed by the action of the water, into an acid salt which dissolves in the water, and a basic salt which produces a precipitate and makes the liquid milky. When a sufficient quantity of nitric acid is added, the solution is completely effected, and the liquid remains clear. The reagents then produce the following appearances.

A solution of *Potash* produces a white precipitate, which is insoluble in an excess of the precipitant.

Ammonia acts in the same manner.

A solution of *Carbonate of Potash* produces a white precipitate, which is likewise insoluble in an excess of the precipitant.

A solution of *Bicarbonate of Potash* produces a similar precipitate, with a disengagement of carbonic acid gas.

A solution of *Carbonate of Ammonia* behaves in the same manner.

A solution of *Phosphate of Soda* produces a white precipitate.

A solution of *Oxalic Acid* produces no immediate precipitate; but after some time, a crystalline precipitate is perceptible.

A solution of *Prussiate of Potash* produces a white precipitate, which is insoluble in muriatic acid.

A solution of *Red Prussiate of Potash* produces a pale yellow precipitate, which is soluble in muriatic acid.

Hydrosulphuret of Ammonia produces a black, or in small quantities, a very dark brown precipitate, which is insoluble in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas* produces a black precipitate, even in the acid solutions. When but a small quantity of oxide of bismuth is contained in the solution, the colour of the precipitate is dark brown. It is easily reduced to metallic bismuth, when mixed with soda, and fused on charcoal in the inner flame of the blowpipe.

A bar of *Metallic Zinc* precipitates bismuth from its solutions, and even from the milky liquor produced by diluting the solutions of oxide of bismuth with water, in the metallic state, and in the form of a black spongy mass.

The solutions of oxide of bismuth can also be recognised by the following reagents.

A solution of *Iodide of Potassium* produces in bismuth oxide solutions, a brown precipitate, which readily dissolves in an excess of the precipitant.

A solution of *Chromate of Potash* produces in solutions of oxide of bismuth, a yellow precipitate, which is soluble in diluted nitric acid.

The salts of oxide of bismuth cannot be heated to redness, in contact with the air, without undergoing decomposition.

The solutions of the salts of oxide of bismuth, which can only be solutions of acid salts, redden litmus paper.

The salts of oxide of bismuth which are insoluble in water, dissolve in acids. The acid solutions become milky on the addition of water. They give with liquid sulphuretted hydrogen a dark brown or black precipitate, which is easily reduced to beads of metallic bismuth when heated with soda on charcoal before the blowpipe.

Before the *Blowpipe,* the salts of oxide of bismuth can be easily recognised. When mingled with soda, and heated in the inner flame, they are easily reduced, and afford globules of metallic bismuth, which are brittle, and spring to pieces under the hammer. During the operation, the charcoal becomes coated with a yellow powder. (BERZELIUS: *Anwendung des Löthrohrs,* p. 95.)

The salts of oxide of bismuth can be readily recognised from their behaviour with water, and with hydrosulphuret of ammonia. From solutions of protoxide of lead, they are easily distinguished by their reaction with a solution of potash, and also by giving no precipitate with diluted sulphuric acid. The metallic globules obtained by reduction with the blowpipe, are discriminated from those afforded by the reduction of lead salts, by their brittleness.

The presence of non-volatile organic substances does not hinder the precipitation of oxide of bismuth, either by water or by alcalies.

XXIII. DEUTOXIDE OF COPPER.

The deutoxide of copper is pulverulent, and of a black colour. It is fused by exposure to a very strong heat. When heated with charcoal, or with organic bodies, it is easily reduced, either to protoxide of copper, or to reguline copper. It readily dissolves in acids. The solution has generally a blue colour. When, however, the solution is effected in muriatic acid, it possesses an emerald-green colour. The hydrate of the deutoxide of copper is blue; but, upon being dried, or upon being exposed to the heat of boiling water, it loses its water, and becomes black.

A solution of *Potash* produces, in solutions of deutoxide of copper, a voluminous blue precipitate of hydrate of deutoxide. When this is boiled with an excess of potash, it turns black, and quickly subsides. It is then in the state of deutoxide. If a solution of deutoxide of copper be boiled with a smaller quantity of potash than is necessary to decompose it completely, the operator obtains, not a black, but a light green precipitate, which is a basic salt of the deutoxide.

Ammonia, added in small quantity to solutions of deutoxide of copper, produces a greenish precipitate, which, however, dissolves very easily in an excess of the precipitant, and produces a blue solution. The colour of this blue ammoniacal solution is much darker than that produced, when, instead of deutoxide of copper, a similar quantity of oxide of nickel is dissolved in an excess of ammonia. Even when a solution of copper is so much diluted that it appears colourless, it acquires a bluish colour from caustic ammonia. In an ammoniacal solution of deutoxide of copper, no immediate precipitate is produced, in the cold, by the addition of a solution of pure potash: but, after a while, if the solution be not too dilute, a blue precipitate makes its appearance. If, however, the ammoniacal solution of deutoxide of copper be boiled with a solution of caustic potash, a dense black precipitate is formed. When this precipitate has fully subsided, the solution, which was previously of a deep blue colour, is found to be colourless.

A solution of *Carbonate of Potash* produces, in solutions of deutoxide of copper, in the cold, a blue precipitate, which boiling renders black and dense.

A solution of *Bicarbonate of Potash* gives, with solutions of deutoxide of copper, a light greenish precipitate, which completely dissolves in an excess of the precipitant, and forms a light bluish solution.

A solution of *Carbonate of Ammonia*, in small quantity, produces a light greenish precipitate, which is dissolved by a greater quantity of the precipitant. The solution so produced, has the same blue colour as the solution formed by the addition of pure ammonia to a solution of deutoxide of copper.—A solution of pure potash occasions here also, by boiling, a heavy black precipitate.

A solution of *Phosphate of Soda* produces, in solutions of deutoxide of copper, a greenish-white precipitate, which dissolves in ammonia, and forms a blue solution. By the addition of potash to the ammoniacal solution, and by boiling it, a black heavy precipitate is produced.

A solution of *Oxalic Acid* produces immediately, in a neutral solution of deutoxide of copper, a greenish-white precipitate.

A solution of *Prussiate of Potash* gives, with solutions of deutoxide of copper, a reddish-brown precipitate, which is insoluble in muriatic acid.

A solution of *Red Prussiate of Potash* produces, in solutions of deutoxide of copper, a yellowish-green precipitate, which is insoluble in muriatic acid.

Hydrosulphuret of Ammonia produces, in neutral solutions of deutoxide of copper, a black, in small quantities a dark brown, precipitate, which is insoluble in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas,* produces a black, in small quantities a dark brown precipitate, in solutions, both neutral and acid, of deutoxide of copper.

A bar of *Metallic Zinc* precipitates copper from its solutions, in the form of a black coating.—*Metallic Iron* precipitates copper, with the peculiar colour of copper. Even a very slight trace of copper can be precipitated from its solutions by clean iron, upon which it produces a copper-coloured coating.

The solutions of deutoxide of copper can also be distinguished by the following reagents:

A solution of *Iodide of Potassium* produces, in solutions of deutoxide of copper, a white precipitate, the colour of which can only be properly examined, when the coloured solution, which then contains free iodine, is poured off. An excess of the iodide of potassium redissolves the precipitate.

A solution of *Chromate of Potash* gives, with solutions of deutoxide of copper, a reddish-brown precipitate. This readily dissolves in ammonia, and forms an emerald-green solution. It is also easily soluble in diluted nitric acid.

The salts of deutoxide of copper which are soluble in water, cannot be heated to redness, in contact with the air, without being decomposed: yet, if the heat be not too strong, the sulphate of copper escapes decomposition.

The solutions of the neutral salts of deutoxide of copper redden litmus paper.

The salts of deutoxide of copper which are insoluble in water, can be dissolved by free acids. The smallest quantity of deutoxide of copper can be precipitated from the acid solution by liquid sulphuretted hydrogen. The precipitated sulphuret of copper must be examined before the blowpipe.—The acid solution of these compounds is, like solutions of other copper salts, rendered blue by the addition of an excess of ammonia. A smaller quantity of ammonia, so much, for example, as is necessary to saturate the acid, has the effect of precipitating the insoluble salt of deutoxide of copper undecomposed from solution.

Before the *Blowpipe*, the salts of deutoxide of copper can be detected very easily. Dissolved in borax and microcosmic salt, they produce in the outer flame, a fine green colour; in the inner flame, a dirty-brownish red. When the quantity of the copper salt is very small, the reddish-brown colour is easily produced by the addition of tin. Mingled with soda, and exposed on charcoal, to the inner flame, they are reduced: even the smallest portions of a copper salt can be detected by the particles of metal having the peculiar colour of copper, which are found on washing away the charcoal. (BERZELIUS: *Anwendung des Löthrohrs*, p. 99.)

The solutions of deutoxide of copper can very easily be recognised by their behaviour with ammonia, with a solution of prussiate of potash, and with hydrosulphuret of ammonia. They are distinguished from nickel solutions by their behaviour towards the solution of potash, and liquid sulphuretted hydrogen.

The presence of non-volatile organic substances in solutions of deutoxide of copper has a remarkable influence over the behaviour of that compound towards reagents. When the solution of deutoxide of copper is only slightly coloured by organic matter, the addition of an excess of potash produces no precipitate. The solution, however, acquires a blue colour, similar to that produced in common solutions of deutoxide of copper by an excess of ammonia. This is the case, for example, when white wine, or a solution of sugar or of tartaric acid, contains a not inconsiderable quantity of blue vitriol, of verdigris, or of any other salt of copper. The more deutoxide of copper the solution contains, the more brilliant is the resulting blue colour. When a blue alcaline cupreous solution of this sort is boiled, the deutoxide of copper is, in most cases, reduced, and a yellowish-brown or reddish-brown precipitate is formed, which precipitate is hydrate of protoxide of copper. Frequently, the copper is almost wholly precipitated in the state of protoxide. This is the case, for example, when white wine which has been adulterated by a copper salt, is treated as described above. Often, however, the liquid continues blue after the boiling, and in that case, only a portion of the copper has been precipitated in the state of protoxide. This is the case when cupreous sugar solutions are thus treated. Cases also occur, in which boiling produces no change in the blue solution; this happens with cupreous tartaric acid solutions.—When these solutions contain but slight traces of deutoxide of copper, its presence cannot be detected by a solution of potash; for this reagent then produces no blue colour, and boiling produces no precipitate of protoxide. And when also the cupreous solution is very deeply coloured by organic substances, no blue colour can be produced by potash; this is the case with red wine which contains a large quantity of deutoxide of copper. The addition of potash to such a solution produces a dirty green opaque solution, and a precipitate of the same colour. Boiling, however, has the effect of throwing down brownish-red protoxide of copper.

If ammonia be added to a solution of copper which is contaminated by non-volatile organic substances, no blue colour is communicated to the solution, unless the quantity of the deutoxide of copper be pretty considerable, and the colour of the liquid be not dark. When, for example, white wine contains a pretty large quantity of deutoxide of copper, the addition of an excess of ammonia produces merely a dirty green or brown colour, and a blue solution can be produced only when the quantity of dissolved deutoxide of copper is very considerable. When the solution of deutoxide of copper is strongly coloured by organic substances, then an excess of ammonia produces no blue colour, even though a pretty large quantity of deutoxide of copper be present. Red wine, which contains deutoxide of copper, acquires from ammonia only a dirty brown colour, a change precisely similar to that produced by ammonia in perfectly pure red wine.

One of the most trust-worthy reagents for readily detecting deutoxide of copper in solutions which contain a large quantity of non-volatile organic substances, is the solution of prussiate of potash. Even when the slightest traces of deutoxide of copper are contained in a solution with very considerable quantities of organic substances, the solution of prussiate of potash produces the same characteristic reddish precipitate that it produces in solutions of pure deutoxide of copper. It is necessary, however, that the solution be either neutral or slightly acid, and not alcaline. Slight traces of deutoxide of copper can be detected in this manner in white wine, and in solutions of sugar and other organic substances. The solutions, however, must not be very strongly coloured, otherwise the test becomes ineffectual. In red wine, for example, it is impossible to detect deutoxide of copper by prussiate of potash, unless the deutoxide of copper be present in considerable quantity.

The surest way of detecting the slightest traces of deutoxide of copper in a solution, is to precipitate it in the state of metallic copper, by clean iron, as, for example, by the blade of a knife. Even when the solution contains organic substances of every description, and is quite darkly coloured, or even completely opaque, the presence of the slightest traces of deutoxide of copper are detected by the copper-red coating acquired by the iron. The only precaution necessary to be taken is, that of rendering the solution slightly acid. When the solution contains but a very small quantity of deutoxide of copper, the iron does not become coated with the metallic copper till it has been exposed to the solution for several hours. This method of detecting small quantities of deutoxide of copper is even more delicate than that by means of sulphuretted hydrogen gas. Solutions which contain very small quantities of deutoxide of copper mingled with large quantities of organic substances, afford, indeed, a brown, but not a black, precipitate with liquid sulphuretted hydrogen. They afford also the same precipitate with hydrosulphuret of ammonia, provided they have been rendered alcaline previous to its addition. But it is necessary that the operator convince himself of the actual presence of copper in the resulting precipitate; he must, therefore, collect and examine it before the blowpipe. This, however, is not easy to do. Small quantities of sulphuret of copper are separated by the filter with the greatest difficulty; and, in solutions, which contain much organic matter, are retained a very long time in suspension. Extremely slight traces of copper are, besides, frequently not at all indicated by liquid sulphuretted hydrogen, while they can still be precipitated by blank iron; and when, moreover, a solution is very strongly coloured, the employment of liquid sulphuretted hydrogen for the detection of copper, is altogether objectionable.

When pasty or solid organic substances are mingled with small quantities of deutoxide of copper, they are usually digested with nitric acid, and in some cases, with diluted sulphuric acid, and the deutoxide of copper is sought for in the filtered solution. Extremely slight traces of deutoxide of copper, when mingled with very large quantities of organic substances, cannot, however, be detected by such a process. It is best, in this case, to mix the substance with carbonate of soda or carbonate of potash, to ignite the mixture in a Hessian crucible, and to levigate the ignited mass. The charcoal is then separated by washing, and the reduced copper remains in the mixture. In this manner, copper can be detected in food which has been boiled in copper vessels, and in bread which has been adulterated with very small quantities of blue vitriol.—The best method of performing this operation so as to detect the slightest trace of copper, has been described by JACQUEMYNS (POGGENDORFF's Annalen, T. XVIII. p. 75), as follows: The substance is mixed with a sufficient quantity of water to produce a soft paste, which is then mixed with twice its weight of pulverised crystals of carbonate of soda. The Hessian crucible which contains the mixture is covered and gradually heated; and, finally, is exposed during a quarter of an hour to a full red heat. After becoming cold, the charred mass is pulverised in an agate mortar. A portion of the mass is first placed in the mixture, and after being moistened with water, is very finely pulverised; more water is then poured into the mortar, and after being stirred round with the pestle, is carefully poured off with the charcoal powder in suspension. The remainder of the mass is then pulverised in the same manner, and the grinding and washing is continued until the mortar is entirely freed from charcoal. The copper should then remain at the bottom of the mortar, in the state of minute metallic copper coloured scales.—If a smaller quantity of carbonate of soda be taken than that which is here prescribed, the deutoxide of copper can still be reduced, but it is then so finely divided, that it is liable to be washed away with the charcoal. It is necessary also to allow the crucible to be thoroughly ignited, that the minute particles of the reduced copper may be better able to unite together. To prevent the destruction of the crucible by the alcaline carbonate in the heat, it is proper to lay at the bottom of the crucible a portion of the substance for analysis, unmingled with carbonated alcali. A mortar of porcelain or stone cannot be employed instead of an agate mortar.

XXIV. OXIDE OF SILVER.

In a pure state, the oxide of silver forms a greyish brown powder. It turns black in the sunshine, and is reduced by ignition to metallic silver. It readily dissolves in nitric acid and in several other acids. The acid solution behaves towards reagents like the aqueous solutions of the salts of oxide of silver.

A solution of *Potash* produces in solutions of oxide of silver, a light brown precipitate, which is insoluble in an excess of the precipitant, but is dissolved when ammonia is added.

Ammonia produces, in neutral solutions of oxide of silver, when added in very small quantity, a brown precipitate, which is dissolved with extreme facility when a little more ammonia is added. If the solution of oxide of silver contains free acid, the saturation by caustic ammonia produces no precipitate.—In a solution of oxide of silver, to which ammonia has been added in excess, a solution of pure potash produces a white precipitate, provided the excess of ammonia be very small.

A solution of *Carbonate of Potash* produces in solutions of oxide of silver, a white precipitate, which is soluble in ammonia.

A solution of *Bicarbonate of Potash* produces in solutions of oxide of silver, a white precipitate, which is soluble in ammonia.

A solution of *Carbonate of Ammonia* produces in solutions of oxide of silver, a white precipitate, which is soluble in an excess of the precipitant.

A solution of *Phosphate of Soda* produces in neutral solutions of oxide of silver, a yellow precipitate, which is soluble in caustic ammonia. The solution remaining above the precipitate reddens litmus paper.—If the phosphate of soda be exposed, shortly before the experiment, to a strong red heat, and then dissolved in water, its solutions produces in solutions of oxide of silver, a white precipitate.

A solution of *Oxalic Acid* produces in neutral solutions of oxide of nickel, a white precipitate, which is soluble in ammonia.

A solution of *Prussiate of Potash* produces in solutions of oxide of silver, a white precipitate.

A solution of *Red Prussiate of Potash* produces in solutions of oxide of silver, a reddish brown precipitate, which has much resemblance with that thrown down by ammonia from solutions of peroxide of iron.

Hydrosulphuret of Ammonia produces in solutions of the salts of oxide of silver, a black precipitate, which is insoluble in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas,* produces either in neutral or acid solutions of oxide of silver, a black precipitate.

A bar of *Metallic Zinc* precipitates silver from its solutions in the metallic state. Near the zinc, the reduced silver is black; farther therefrom, it is white.

The solutions of oxide of silver can also be recognised from their behaviour with the following reagents.

Muriatic Acid and solutions of the *Chlorides* produce a white precipitate, even in very dilute solutions of the oxide of silver. When the solution contains an extremely small quantity of oxide of silver, the precipitate subsides very slowly, and the solution acquires an opalescent appearance. In larger quantities, the precipitate is flocculent. It is readily dissolved by ammonia, but is insoluble in diluted acids. If exposed to the light of the sun, it speedily loses its white colour, and becomes grey or rather violet. The change of colour commences at the surface.

A solution of *Iodide of Potassium* produces in solutions of oxide of silver, a white precipitate inclining to yellow. This is very sparingly soluble in ammonia, but dissolves more easily in an excess of the solution of iodide of potassium.

A solution of *Chromate of Potash* produces in solutions of oxide of silver, a dark reddish brown precipitate, which is soluble in diluted nitric acid and in ammonia.

A solution of *Protosulphate of Iron* produces in neutral solutions of oxide of silver, a white precipitate, consisting of metallic silver.

A solution of *Protochloride of Tin,* to which muriatic acid in sufficient quantity to render it clear has been added, produces in solutions of oxide of silver, when added in small quantity, a white precipitate of chloride of silver. When, however, a greater quantity of protochloride of tin is added to solutions of oxide of silver, the solutions, especially when heated, acquire a brown colour from reduced silver.

The white or light-coloured precipitates of silver are particularly characterised by the black colour which they readily assume at the surface, on being exposed in a moist condition to the influence of light. This change of colour takes place most easily with the precipitates formed in silver solutions by muriatic acid and the chlorides; it occurs in a less degree, or scarcely at all, with those produced by solutions of iodide of potassium and phosphate of soda.

The salts of oxide of silver which are soluble in water, cannot be heated to redness without being decomposed.

The solutions of the neutral salts of silver have no action on litmus paper.

The salts of oxide of silver which are insoluble in water, nearly all dissolve in nitric acid. The presence of oxide of silver is detected in the acid solution by means of muriatic acid. This reagent precipitates the chloride of silver, which is insoluble in acids.

Before the *Blowpipe*, the silver salts are easily detected by being fused with soda, upon which they are reduced to metallic silver. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 101.)

The solutions of oxide of silver can very easily be recognised by their behaviour towards muriatic acid, and by the behaviour of the precipitated chloride of silver towards ammonia and diluted acids. That which distinguishes the chloride of silver from other insoluble chlorides, being its solubility in ammonia and insolubility in diluted acids.

The presence of non-volatile organic substances in solutions of oxide of silver, does not prevent the precipitation of that metal by muriatic acid.

XXV. OXIDES OF MERCURY.

a. PROTOXIDE OF MERCURY.

Pure protoxide of Mercury is black. A very gentle heat converts it into metallic mercury and peroxide of mercury. A strong heat decomposes it into metallic mercury and oxygen gas. When treated by various acids, and particularly when free alcali is present, the protoxide likewise very often falls into metallic mercury and peroxide. The solution of the protoxide is best obtained by treating an excess of the metal with nitric acid.—Some of the neutral salts of protoxide of mercury dissolve only partially in water, being decomposed into an acid soluble salt, and a basic salt which is not soluble. The neutral nitrate of protoxide of mercury is a salt of this description.

The solutions of protoxide of mercury behave towards reagents as follows:

A solution of *Potash* produces in solutions of protoxide of mercury, a black precipitate, which is insoluble in an excess of the precipitant.

Ammonia produces in solutions of protoxide of mercury, a black precipitate, which is insoluble in an excess of ammonia.

A solution of *Carbonate of Potash* produces in solutions of protoxide of mercury, a dirty yellow precipitate, which boiling renders black.

A solution of *Bicarbonate of Potash* produces a white precipitate, which turns black when boiled. Carbonic acid gas is discharged during the boiling.

A solution of *Carbonate of Ammonia* produces in solutions of protoxide of mercury, in small quantity a grey, in larger quantity a black precipitate.

A solution of *Phosphate of Soda* gives with solutions of protoxide of mercury a white precipitate.

A solution of *Oxalic Acid* produces in solutions of protoxide of mercury, a white precipitate.

A solution of *Prussiate of Potash* produces in solutions of protoxide of mercury a white gelatinous precipitate.

A solution of *Red Prussiate of Potash* produces in solutions of protoxide of mercury, a reddish brown precipitate, which after some time becomes white.

Hydrosulphuret of Ammonia produces immediately, in solutions of protoxide of mercury, a black precipitate, which is not only insoluble in an excess of the precipitant, but also in ammonia. It partially dissolves in a solution of pure potash, leaving a black powder, which on being brought upon a filter and rubbed with a glass rod, proves to be metallic mercury. The filtered alcaline solution, on being supersaturated by an acid, affords a black precipitate of sulphuret of mercury.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas,* produces immediately, either in neutral or acid solutions of protoxide of mercury, a black precipitate.

This is the case even when much less sulphuretted hydrogen gas is employed, than is necessary for the complete saturation of the solution of protoxide of mercury.

A bar of *Metallic Zinc* throws down mercury in the metallic state, in the form of a grey coating, which is an amalgam of zinc and mercury.

The solutions of protoxide of mercury can also be recognised from their behaviour with the following reagents.

Muriatic Acid and solutions of the *Chlorides* produce in solutions of protoxide of mercury, even when added in the smallest quantities, a white precipitate, which is insoluble in simple acids, and is rendered black by ammonia.

A solution of *Iodide of Potassium* produces in solutions of protoxide of mercury, a greenish yellow precipitate, which a greater addition of the reagent renders blackish, and a still greater dissolves.

A solution of *Chromate of Potash* gives a red precipitate with solutions of protoxide of mercury.

A drop of a solution of protoxide of mercury placed upon a piece of bright *copper*, and rubbed off with paper, after having been some time in contact, leaves upon the copper a silvery stain, which disappears when it is heated to redness.

The salts of protoxide of mercury which are soluble in water, are decomposed and volatilized by a red heat.

The solutions of the protosalts of mercury redden litmus paper.

The salts of protoxide of mercury which are insoluble in water, can, for the most part, be dissolved in diluted nitric acid. The acid solution produces with muriatic acid a white precipitate, which ammonia turns black but does not dissolve.

If the protosalts of mercury are mingled with dry soda, placed in a glass tube closed at one end, and heated to redness by the flame of the *Blowpipe*, they are reduced, and mercury sublimes in the form of a grey powder, which on being rubbed together by a glass rod, can easily be seen to form globules of metallic mercury. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 101.)

The solutions of the protosalts of mercury can easily be detected by their behaviour towards muriatic acid, and by the behaviour of the precipitate thus formed towards ammonia. The conversion of its white colour to black, by the action of the latter reagent, is a character which distinguishes the mercurial precipitate from that produced by muriatic acid in the solutions of oxide of silver. In the dry way, it is very easy to prove the presence of mercury, by the production of the globules of that metal.

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b. PEROXIDE OF MERCURY.

Pure peroxide of mercury is commonly crystalline, and then possesses a brick-red colour; but when it is very finely pulverised, it becomes yellowish. A gentle heat turns it black; but the brick-red colour returns as the heat is diminished. A strong heat decomposes it into oxygen gas and metallic mercury.—If peroxide of mercury is supposed to be adulterated with red lead, it should be put into a small glass tube closed at one end, and be exposed to heat till the peroxide of mercury is completely decomposed. If red lead be present, the operation yields fused protoxide of lead.—If peroxide of mercury, adulterated with brick-dust, be treated in the same manner, the brick-dust remains behind unchanged.

Peroxide of mercury easily dissolves in acids. The acid solution behaves towards reagents precisely like solutions of the salts of peroxide of mercury which are soluble in water.

A solution of *Potash* produces in solutions of peroxide of mercury, a yellow precipitate, which is insoluble in an excess of potash. If too small a quantity of the precipitant be applied to the solution of peroxide of mercury, the precipitate is reddish brown.—If the mercurial solution contain muriate of ammonia, potash produces a white precipitate. And when also the solution contains very much free acid, potash produces a whitish precipitate.

Ammonia produces in solutions of the persalts of mercury, a white precipitate, not soluble in an excess of the precipitant.

A solution of *Carbonate of Potash* produces in solutions of peroxide of mercury, a reddish brown precipitate, which is insoluble in an excess of carbonate of potash. If the solution of mercury contain muriate of ammonia, carbonate of potash produces a white precipitate.

A solution of *Bicarbonate of Potash,* added to solutions of pernitrate or persulphate of mercury, produces, under disengagement of carbonic acid gas, a brownish red precipitate. A solution of perchloride of mercury is, at first, not troubled by a solution of bicarbonate of potash; after some time, however, it deposits a dark reddish brown precipitate.

A solution of *Carbonate of Ammonia* produces in solutions of peroxide of mercury a white precipitate.

A solution of *Phosphate of Soda,* added to solutions of pernitrate or persulphate of mercury, produces a white precipitate; but added to solutions of perchloride of mercury, it only occasions a very slight troubling.

A solution of *Oxalic Acid* produces in solutions of pernitrate and persulphate of mercury a white precipitate; but in perchloride of mercury, it forms no precipitate.

A solution of *Prussiate of Potash* produces in solutions of peroxide of mercury a white precipitate, which after some reposure becomes blue, in consequence of the formation of prussian blue.

A solution of *Red Prussiate of Potash* produces in solutions of pernitrate and persulphate of mercury a yellow precipitate; in solutions of perchloride, no precipitate.

Hydrosulphuret of Ammonia, when dropped, in very small quantities, into solutions of peroxide of mercury, produces, where it comes into contact with the liquid, a black precipitate. But this precipitate becomes completely white when the mixture is shaken, even though much of the salt of mercury remains in solution undecomposed. The white precipitate, formed by agitating the black one in the liquid, remains a very long time in suspension. If more hydrosulphuret of ammonia is gradually added to the solution, the resulting precipitate is a mixture of black and white, and if an excess of the precipitant is added, the precipitate, which does not redissolve in the cold, is rendered perfectly black. The precipitate is also insoluble in ammonia, but it dissolves completely in a solution of potash. It can be reprecipitated from the alcaline solution, by supersaturating it with an acid.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas,* behaves both with acid and neutral solutions of peroxide of mercury in the same manner as the preceding reagent, but when sulphuretted hydrogen is employed, the phenomena can be better observed than with hydrosulphuret of ammonia.

Metallic Zinc acts with solutions of the peroxide, in the same manner as with solutions of the protoxide.

The solutions of peroxide of mercury can also be recognised by their behaviour with the following reagents:

A solution of *Iodide of Potassium* produces in solutions of peroxide of mercury a cinnabar red precipitate, which dissolves either in an excess of the iodide of potassium or of the solution of peroxide of mercury. It is also soluble in muriatic acid.

A solution of *Chromate of Potash* produces in solutions of peroxide of mercury, provided they be not very dilute, a yellowish red precipitate.

Towards *Metallic Copper,* solutions of peroxide of mercury behave in the same manner as solutions of the protoxide.

When heated to redness, the persalts of mercury which are soluble in water, are decomposed in the same manner as the soluble protosalts.

Solutions of the neutral persalts of mercury redden litmus paper.

The salts of peroxide of mercury which are insoluble in water, nearly all dissolve in acids. The presence of peroxide of mercury in the acid solution is best detected by a very gradual addition of liquid sulphuretted hydrogen. When a small quantity of this reagent is mingled with an excess of a solution of peroxide of mercury, it produces a white precipitate, which remains a long time in suspension. When an excess of liquid sulphuretted hydrogen is added, the precipitate becomes both black and dense.

Before the *Blowpipe,* the persalts, like the protosalts, are reduced to metallic mercury by being treated with soda.

The salts of peroxide of mercury can be very easily recognised from their behaviour with hydrosulphuret of ammonia, or, as this is too concentrated, better from their behaviour with liquid sulphuretted hydrogen. In the dry way, the operator can easily satisfy himself of the presence of mercury, by the production of the globules of that metal.

The presence of such organic substances as cannot be volatilized without decomposition, has a very considerable influence over the behaviour of solutions of peroxide or perchloride of mercury towards reagents. This is the case even when the solutions are not coloured by the organic matter. If, for example, sugar, or non-volatile organic acids be added to a solution of peroxide of mercury, then the solution, on being tested with an excess of potash, gives no precipitate if but a small quantity of peroxide of mercury be present, or a dirty yellow precipitate if a large quantity of peroxide be present. In both cases, however, the solution, after some time, deposits a heavy black precipitate, which contains a very large quantity of metallic mercury. This black precipitate is immediately produced when the solution is boiled. The same appearances are exhibited when, instead of potash, a solution of carbonate of soda or of potash is employed. Without the addition of an alcali, the reduction to metallic mercury does not take place. Ammonia produces in such solutions of peroxide of mercury a white precipitate, which continues white for a long time, and upon being boiled merely blackens partially.

When solutions of peroxide of mercury are strongly coloured by organic substances;—when, for example, they contain red wine,—they immediately produce with solutions of potash, dark coloured precipitates of various hues. These are turned black by reposure, and still more rapidly by boiling. They contain metallic mercury. White wine containing a large quantity of perchloride of mercury acquires from a solution of potash; a brownish red colour, but affords no immediate precipitate. After some time, however, or more speedily if boiled, this solution produces a dirty brownish red, and finally a grey precipitate.

When hydrosulphuret of ammonia, or liquid sulphuretted hydrogen, is added in excess to solutions of mercury which contain much organic matter, a precipitate of sulphuret of mercury is produced; but when the solutions are strongly coloured, the precipitate is commonly difficult to be seen. That it may be determined with certainty, whether the precipitated sulphuret contains mercury, it must be filtered, dried, mingled with soda in a little glass tube closed at one end, and heated before the blowpipe. If mercury be present, it is reduced and sublimed. But as the presence of certain organic substances has the effect of making the sulphuret of mercury remain a very long time in suspension in the solution, and frequently of partly or totally preventing its filtration, the operator must employ sulphuretted hydrogen as the precipitant, only when the quantity of mercury is very considerable. To detect a very small quantity of mercury in such solutions, it is best to employ blank copperplate. This is placed in the solutions, which must either be neutral or not too strongly acid; though, indeed, the mercury can be precipitated by copper, even from an alcaline solution. The precipitation is also thus effected, even when the solution is very deeply coloured and contains organic substances of every description. The copper, after some time, acquires a grey coating, if the solution contain the slightest traces of mercury. The grey coating, on being rubbed with paper, gives a silvery appearance to the copper, but one which a gentle heat is sufficient to drive away. When the quantity of the mercury in solution is extremely small, the silvery appearance produced upon the copper is less distinct, because the characteristic colour of the copper shines through the thin coating of mercury. In this case, the operator must heat the copper in several spots, and thus restore its own pure colour. The slight silvery appearance on the places which have not been heated, is then rendered more striking by contrast.

When peroxide of mercury is contained in pasty or solid organic substances which are not soluble in water, they are, if possible, to be dissolved in ammonia. The precipitate produced by albumen in solutions of peroxide or perchloride of mercury, is insoluble in water, but easily soluble in ammonia, or in a solution of potash. The mercury can be precipitated from the ammoniacal solution by hydrosulphuret of ammonia; but the sulphuret of mercury remains a very long time suspended in the solution and can scarcely be separated from it. Yet its separation is absolutely necessary, that it may be examined for mercury before the blowpipe. It is therefore much better to place a blank copper plate in the ammoniacal solution, from which, as well as from a neutral or slightly acid solution, the mercury can be precipitated by this metal. The copper acquires a grey surface, which, on being rubbed by paper becomes bright and silvery. Even slight traces of mercury can be thus detected in the ammoniacal solution. It is probable that the presence of mercury in blood, should this fluid contain that metal, could also be best detected by this process; because all the constituents of blood are soluble in an excess of ammonia.

The operator must not employ a solution of potash, instead of ammonia, in these experiments. The presence of mercury cannot be detected in a solution of potash by hydrosulphuret of ammonia; for the resulting sulphuret of mercury remains in solution, if a sufficient quantity of potash be present. Mercury can be precipitated from such a solution by copper plate, yet not so effectually as from an ammoniacal solution.

When the mercurial organic substance is soluble neither in water nor in ammonia, it is customary to digest it with nitric acid, and to seek for the mercury in the nitric acid solution. But this method is often attended by disadvantages, particularly when the quantity of the organic substance is considerable, and that of the mercury very small. It is better in such cases to adopt the process which follows: The dry substance is mingled with about three or four times its weight of carbonate of soda or carbonate of potash, and the mixture is placed in a retort which is large enough to contain four times as much as the bulk of the mixture. A sufficient quantity of water is then added to make the whole into a paste, and the retort is shaken till the dry substance is properly mingled with the water. If the substance for examination is of a pasty consistence, it must be mingled with carbonate of soda and then dried at a very gentle heat, that it may be brought into a fit state to be inserted into the retort. The neck of the retort is then connected, by means of a cork, with a receiver, but the juncture must not be quite air tight. The retort is then gradually heated, and the heat is increased till the bottom of the retort becomes red hot.—When the quantity of the substance for examination is inconsiderable, so that the operation can be performed in a small retort, the heat can be best applied by the flame of a spirit lamp with circular wick; but when the quantity is large, it is necessary, of course, to employ a charcoal fire. The mass in the retort commonly swells up very much, and the operator must take great care that it does not rise into the neck. After the cooling of the apparatus, the neck of the retort is broken off by the application of a hot coal, close to the body; the neck is afterwards split longitudinally, also by applying a hot coal. The interior of the neck is found to be covered with a glutinous brown empyreumatic oil, and at about an inch from the body of the retort, a quantity of minute globules of mercury are observable. The existence of these mercurial globules is demonstrated with most certainty, by rubbing the finger on the place where they appear to be fixed, and then examining the substance which is transferred to the finger. The globules of mercury can easily be recognised upon the finger, by the unassisted eye, or still better when a lens is employed. It is necessary to remove the globules from the glass prior to examination, lest the eye should be deceived; for small air bubbles fixed in the glutinous oil on the glass can easily be mistaken for globules of mercury.—When the organic substance contained but a small quantity of mercury, the whole of the latter remains in the neck of the retort, and none passes with the empyreumatic oil into the receiver. When no globules of mercury have been produced by this experiment, the operator may digest the oil which is in the receiver, together with that which remains in the broken neck of the retort, in nitric acid, and test the nitric acid solution for mercury. When, however, the preceding operation has been conducted with great care, and no mercury is deposited in the neck of the retort, it is seldom that its presence can be detected in the nitric acid solution.

XXVI. OXIDE OF PLATINUM.

Oxide of platinum, in a state of purity, never occurs in analyses. Its hydrate is a yellow powder, which on being heated turns dark brown or nearly black, and disengages water. When more strongly heated, it yields oxygen gas, and is reduced to metallic platinum.—The chloride which corresponds to the oxide forms a dark reddish brown saline mass, which on being heated at about the temperature of melting lead, is reduced to subchloride of platinum, and upon being still more powerfully heated, is reduced to metallic platinum; while in both cases, chlorine gas is disengaged. When the chloride is heated less powerfully than is necessary to convert it entirely into subchloride, it afterwards dissolves completely in water, producing a brown solution of so dark a colour as to appear opaque. According to MAGNUS, this solution contains subchloride of platinum dissolved in chloride of platinum.

The chloride of platinum dissolves in water and in alcohol, producing a dark brown solution. The aqueous solution behaves towards reagents like the solution of platinum in aqua regia, which contains chloride of platinum.

A solution of *Potash* produces a yellow precipitate of chloride of potassium and platinum, particularly when muriatic acid is added, to convert the potash into chloride of potassium. The precipitate is not sensibly soluble in free acids, but it dissolves when heated in an excess of potash, and does not again precipitate when the liquid is cold. When, however, the solution is supersaturated by muriatic acid, the precipitate reappears.

Ammonia produces in solutions of chloride of platinum, a yellow precipitate similar to that produced by potash, particularly when muriatic acid is added to convert the ammonia into muriate of ammonia. This yellow precipitate is insoluble in free acids, but it dissolves when heated in an excess of ammonia, and when the resulting solution is supersaturated by muriatic acid, a white precipitate is produced.

A solution of *Carbonate of Potash* produces in solutions of chloride of platinum a yellow precipitate of chloride of potassium and platinum, particularly when muriatic acid is added to convert the potash into chloride of potassium. This precipitate does not dissolve on being heated in an excess of carbonate of potash.

A solution of *Bicarbonate of Potash* behaves in the same manner.

A solution of *Carbonate of Soda* occasions no precipitation.

A solution of *Carbonate of Ammonia* behaves towards solutions of chloride of platinum, in the same manner as a solution of carbonate of potash.

A solution of *Phosphate of Soda* produces no precipitate in solutions of chloride of platinum.

A solution of *Oxalic Acid* produces no precipitate in solutions of chloride of platinum.

A solution of *Prussiate of Potash* produces in solutions of chloride of platinum, a precipitate of chloride of potassium and platinum, while the solution becomes somewhat darker in colour.

A solution of *Red Prussiate of Potash* behaves in the same manner as the solution of prussiate of potash.

A solution of *Cyanuret of Mercury* produces no precipipitate in solutions of chloride of platinum.

A solution of *Protonitrate of Mercury* produces in solutions of chloride of platinum a considerable yellowish red precipitate.

A solution of *Protosulphate of Iron* produces no precipitate in solutions of chloride of platinum.

Protochloride of Tin communicates to solutions of chloride of platinum a deep reddish brown colour, without producing a precipitate.

A solution of *Iodide of Potassium* communicates to solutions of chloride of platinum a deep reddish brown colour, and produces a brown precipitate, but of a lighter colour than the solution. If the solution is exposed to heat, the glass acquires a metallic coating.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas*, produces in acid and neutral solutions of chloride of platinum, at first merely a change of the colour to brown, but after some time a brown precipitate, which upon subsiding appears black.

Hydrosulphuret of Ammonia produces in solutions of chloride of platinum a brownish black precipitate, which dissolves in a pretty large excess of the precipitant. The solution has a deep reddish brown colour.

A bar of *Metallic Zinc* precipitates platinum from its solutions, in the state of a black metallic powder.

The compounds of oxide and chloride of platinum are decomposed by ignition. They leave metallic platinum, while the acid, if it be volatile, flies off in the gaseous state with the oxygen or the chlorine of the compound. If the compound of chloride of platinum contain a metallic chloride, both non-volatile and indecomposable by heat, then the latter remains behind after the ignition, mingled with finely divided platinum.

Solutions of the compounds of oxide of platinum redden litmus paper; but solutions of the compounds of chloride of platinum leave the blue litmus paper unchanged.

The compounds of platinum which are insoluble in water must be ignited. The oxide or chloride is then reduced to metallic platinum, which can be dissolved in aqua regia. It is then easy to detect the presence of platinum in the acid solutions, by means of the above-cited reagents.

Before the *Blowpipe*, the compounds of platinum are completely reduced, and communicate no colour to the fluxes.

The compounds of oxide and chloride of platinum are very easily distinguished by the precipitates which their solutions produce with potash and ammonia. They are distinguished by this character from all other substances. When the solution of platinum is acid, it is only necessary to add pure or carbonated potash or ammonia, to produce the yellow precipitate. When the solution is neutral, it is necessary either to add a concentrated solution of chloride of potassium or muriate of ammonia, or when carbonated alcalies are employed, to acidulate the solution with muriatic acid.

The presence of non-volatile organic substances in the solution of platinum, if they are not in too large a quantity, does not prevent the production of the yellow precipitate by potash. But when too large a quantity of organic matter is present, the addition of potash causes the solution, after some exposure, to become quite black, so that the production of the yellow chloride of potassium and platinum cannot be distinctly observed. If the solution of a compound of chloride of platinum is mixed with alcohol and exposed to a prolonged digestion at a gentle heat, until the alcohol is almost entirely expelled, the resulting aqueous solution, upon being mingled with a solution of cyanuret of mercury, affords a white precipitate, if not immediately, yet after some delay. The quantity of this precipitate is increased, when the whole is allowed to repose. As solutions of platinum which are free from organic matter produce no precipitate with cyanuret of mercury, it is possible to mistake an impure solution of platinum for a solution of palladium; but when the precipitate of platinum is dried and ignited, it is converted into metallic platinum, which, on being dissolved in aqua regia, and tested by the usual reagents, can be recognised with facility.

XXVII. OXIDES OF GOLD.

a. SUBOXIDE OF GOLD.

The suboxide of gold is prepared from the corresponding subchloride, by means of a solution of potash; but its existence is of short duration, for it speedily falls into metallic gold and oxide of gold. The subchloride of gold is, in a similar manner, decomposed by water into metallic gold and chloride of gold.

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b. OXIDE OF GOLD.

The hydrate of the oxide of gold is yellowish-brown. When the oxide of gold is precipitated from the solution of chloride of gold by a base, it always contains a portion of the base employed as the precipitant. It is decomposed by ignition, into metallic gold and oxygen gas. The chloride which corresponds to the oxide is contained in the solution of gold in aqua regia. When heated at the temperature of melting tin, it is converted into subchloride; when heated more powerfully, it is converted into metallic gold.

A solution of *Potash,* added in excess to a solution of chloride of gold, produces at first no precipitate; after some time, the solution acquires a greenish colour, and deposits an inconsiderable black precipitate.

Ammonia produces in solutions of chloride of gold, a yellow precipitate.

A solution of *Carbonate of Potash* produces no precipitate in solutions of chloride of gold.

A solution of *Bicarbonate of Potash* produces no precitate.

A solution of *Carbonate of Ammonia* produces in neutral solutions of chloride of gold, a yellow precipitate, under disengagement of carbonic acid gas.

A solution of *Phosphate of Soda* produces no precipitate.

A solution of *Oxalic Acid* produces in solutions of chloride of gold, a dark greenish-black colour, which is owing to the presence of metallic gold. After some time, the metallic gold subsides. When the solution is heated, this change takes place more rapidly, and under disengagement of carbonic acid gas.

A solution of *Prussiate of Potash* communicates to solutions of chloride of gold, an emerald-green colour.

A solution of *Red Prussiate of Potash* produces no precipitate.

A solution of *Cyanuret of Mercury* produces no precipitate in the solution of chloride of gold.

A solution of *Protonitrate of Mercury* immediately produces a black precipitate in the solution of chloride of gold.

A solution of *Protosulphate of Iron* produces in very dilute solutions of chloride of gold, first a blue colouring, and thereafter a precipitate of brown-coloured metallic gold. The solution of protosulphate of iron produces a dark brown precipitate of metallic gold immediately, when the gold solution is not too dilute.

A solution of *Protochloride of Tin,* to which so much muriatic acid has been added that it has become clear, communicates to the most diluted solution of chloride of gold, a reddish-purple colour: in concentrated solutions of gold, this reagent produces a dark reddish-purple precipitate, which is insoluble in free muriatic acid.

A solution of *Iodide of Potassium* communicates a black colour to solutions of chloride of gold: subsequently, a yellowish-green precipitate subsides, leaving free iodine dissolved in the solution.

Hydrosulphuret of Ammonia produces in neutral solutions of chloride of gold, a dark brown precipitate, which completely redissolves in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas,* produces in neutral and acid solutions of chloride of gold, a black precipitate.

A bar of *Metallic Zinc* precipitates gold from its solutions, in the metallic state, and in the form of a brown bulky coating.

The compounds of gold are decomposed when heated to redness, the metal being reduced.

The neutral solution of gold reddens litmus paper.

Solutions of gold are easily recognised from their behaviour towards solutions of protosulphate of iron, of oxalic acid, and of protochloride of tin.

Organic substances have the property of decomposing the compounds of gold, and of precipitating that metal in the reguline state, from its solutions. The reduction of gold is effected more rapidly by some organic substances than by others.

XXVIII. OXIDES OF TIN.

a. PROTOXIDE OF TIN.

Pure protoxide of tin is a greyish-black powder, which, on being brought into contact with ignited bodies, in the open air, takes fire, and becomes oxidised into peroxide of tin. The hydrate of the protoxide is white, and is more easily soluble in acids than the protoxide itself is, after having been ignited in closed vessels. The protochloride of tin, which corresponds to the protoxide of tin, does not dissolve in water, without undergoing decomposition. It forms a milky solution, in consequence of the production of an insoluble compound of protochloride with protoxide.

The solutions of protoxide of tin in acids, and of protochloride of tin in water, acidulated by a quantity of muriatic acid sufficient to render it clear, behave towards reagents as follows:

A solution of *Potash* produces a white precipitate, which dissolves in an excess of the precipitant. The solution, after some reposure, but more rapidly when boiled, is decomposed in such a manner as to produce metallic tin in black powder, and a soluble compound of peroxide of tin with potash.

Ammonia produces, in solutions of protoxide of tin, a white precipitate, which is insoluble in an excess of ammonia.

A solution of *Carbonate of Potash* produces, in solutions of protoxide of tin, a white precipitate, which is insoluble in an excess of the precipitant.

A solution of *Bicarbonate of Potash* acts in the same manner.

A solution of *Carbonate of Ammonia* produces, in solutions of protoxide of tin, a white precipitate, which is insoluble in an excess of carbonate of ammonia.

A solution of *Phosphate of Soda* produces, in solutions of protoxide of tin, a white precipitate.

A solution of *Oxalic Acid* produces, in solutions of protoxide of tin, a white precipitate.

A solution of *Prussiate of Potash* produces, in solutions of protoxide of tin, a white gelatinous precipitate.

A solution of *Red Prussiate of Potash* affords a white precipitate, which is soluble in free muriatic acid.

Hydrosulphuret of Ammonia produces, in solutions of protoxide of tin, a brown precipitate, which a very great excess of the precipitant redissolves, especially when this precipitant possesses a yellow colour, occasioned by its containing an excess of sulphur. Muriatic acid, added in excess to the sulphuretted solution, produces a yellow precipitate.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas* produces, in neutral and acid solutions of protoxide of tin, a dark brown precipitate.

A bar of *Metallic Zinc* precipitates tin from the solutions of its protosalts, in the metallic state, and in the form of small greyish-white spangles.

A solution of *Iodide of Potassium* produces, in solutions of protoxide of tin, a flocculent precipitate, the colour of which is white, slightly inclining to yellowish. After a short time, and when the solution is at a certain degree of concentration, the colour becomes cinnabar red. A great excess of iodide of potassium dissolves this precipitate.

The salts of protoxide of tin are decomposed when heated to redness in contact with the air.—Their solutions redden litmus paper.

The salts of protoxide of tin which are insoluble in water, nearly all dissolve in muriatic acid, unless they have been exposed to ignition. The presence of the protoxide of tin in the resulting acid solution, is detected either by liquid sulphuretted hydrogen, or by a solution of gold.

Before the *Blowpipe,* the tin, in the protosalts of tin, is easily reduced. The salts are mingled with soda, and heated on charcoal, in the inner flame. The reduced metallic globule can be recognised as tin, by its allowing itself to be flattened by the hammer, and by its possessing the power, when added to a bead formed of microcosmic salt and copper, of depriving the bead of its green colour, and of rendering it opaque and brownish-red. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 97.)

Solutions of protoxide of tin are very easily known by their behaviour with solution of gold (page 141).

The presence of non-volatile organic substances can sometimes prevent the precipitation of protoxide of tin by alcalies.

b. PEROXIDE OF TIN.

Pure peroxide of tin has, after ignition, a white or yellowish colour. The peroxide of tin which occurs in nature, commonly possesses a dark colour, in consequence of the presence of unessential constituents. Ignited peroxide of tin is completely insoluble in acids, and can only be brought into a soluble state, by being fused with carbonate of potash or of soda. When pure, it is infusible by heat, unless the heat be exceedingly powerful; but it readily fuses with basic substances to an enamel.—The hydrate which is produced by treating metallic tin with nitric acid, is white, and in almost all acids, is either quite insoluble, or but very sparingly soluble. The hydrate of peroxide of tin, prepared by precipitating a solution of perchloride of tin by ammonia, is, on the contrary, soluble in acids. The solutions of peroxide of tin behave towards reagents as follows:

A solution of *Potash* produces, in solutions of the salts of peroxide of tin, a white precipitate, which is soluble in an excess of the precipitant.

Ammonia produces, in solutions of salts of peroxide of tin, a white precipitate, which is completely soluble in a great excess of ammonia.

A solution of *Carbonate of Potash* produces in neutral solutions of the salts of peroxide of tin, under disengagement of carbonic acid gas, a white precipitate, which is completely soluble in an excess of carbonate of potash. This solution, however, after some reposure, again deposits a white precipitate.

A solution of *Bicarbonate of Potash* produces, under disengagement of carbonic acid gas, a white precipitate, which does not redissolve in an excess of the precipitant.

A solution of *Carbonate of Ammonia* behaves in the same manner.

A solution of *Phosphate of Soda* produces in solutions of peroxide of tin, a white precipitate.

A solution of *Oxalic Acid* produces in solutions of peroxide of tin, no precipitate.

A solution of *Prussiate of Potash* produces in solutions of persalts of tin, no immediate precipitate. After some time, a white troubling is visible, and when the mixture has reposed still longer, the whole congeals to a thick, stiff, yellowish jelly, which is insoluble in muriatic acid. In diluted solutions of the persalts of tin, a solution of prussiate of potash does not produce the jelly till after a much longer time.

A solution of *Red Prussiate of Potash* produces in solutions of persalts of tin, no precipitate.

Hydrosulphuret of Ammonia produces in neutral solutions of peroxide of tin, a yellow precipitate, which completely redissolves in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas* produces in neutral or acid solutions of peroxide of tin, no immediate precipitate. After some time a yellow precipitate is formed, the quantity of which increases on longer reposure. This yellow precipitate appears sooner, when a solution of peroxide of tin is boiled with liquid sulphuretted hydrogen.

A bar of *Metallic Zinc* produces in solutions of the persalts of tin, under disengagement of hydrogen gas, a white gelatinous precipitate, which is peroxide of tin.

A solution of *Iodide of Potassium* produces no precipitate in solutions of peroxide of tin.

The salts of peroxide of tin are decomposed when heated to redness.—Their solutions redden litmus paper.

The compounds of peroxide of tin which are insoluble in water, are (previous to ignition) soluble in muriatic acid. The presence of peroxide of tin in the acid solution, is best detected by the yellow precipitate produced by sulphuretted hydrogen gas, which precipitate is insoluble in hydrosulphuret of ammonia. When the compound of peroxide of tin has been ignited, and by that means rendered insoluble in muriatic acid, it must be fused in a platinum crucible, with twice or thrice its weight of dry carbonate of potash or carbonate of soda; after which, the fused mass can be dissolved in diluted muriatic acid, and the presence of peroxide of tin can be detected in the acid solution, in the manner described above.—It will be understood, of course, that this analysis can be of use only when the peroxide of tin is combined with an acid which cannot be precipitated by sulphuretted hydrogen gas.—It is easier, however, to detect the presence of peroxide of tin in these insoluble compounds, by an experiment with the blowpipe.

Before the *Blowpipe*, metallic tin can be obtained by reduction, with the same facility from the persalts as from the protosalts of tin.

Solutions of persalts of tin can be readily known, from their behaviour with liquid sulphuretted hydrogen, and with hydrosulphuret of ammonia. Persalts of tin are best discriminated from salts which contain arsenic acid, by their behaviour before the blowpipe.

The presence of non-volatile organic substances can often prevent the precipitation of peroxide of tin by alcalies.

XXIX. PROTOXIDE OF ANTIMONY.

The protoxide of antimony, in a state of purity, is white. When exposed to heat, it fuses to a yellow mass, which on cooling, becomes greyish-white and crystalline. When heated out of contact with air, it can be completely volatilized; the sublimate then obtained is in the form of brilliant needle-formed crystals. When heated in the open air, it gives out a white smoke, and is partly converted into antimonious acid. It is easily reduced to metallic antimony by ignition with charcoal. On being fused with sulphuret of antimony, it readily produces a red glass. It is insoluble in nitric acid, but is dissolved by muriatic acid. The resulting solution becomes milky on being diluted with water. When a diluted acid has been added to the milky solution, in quantity sufficient to render it clear, the resulting acid solution behaves towards reagents as follows:

A solution of *Potash* produces a white precipitate, which is insoluble in an excess of potash.

Ammonia acts in the same manner.

A solution of *Carbonate of Potash,* the same.

A solution of *Bicarbonate of Potash,* the same.

A solution of *Carbonate of Ammonia,* the same.

A solution of *Phosphate of Soda* produces also a white precipitate.

A solution of *Oxalic Acid,* the same. The two last precipitates, however, could just as well be produced by the water contained in the precipitants.

A solution of *Prussiate of Potash* produces a white precipitate, which is insoluble in muriatic acid, and therefore not occasioned merely by the water of the reagent.

A solution of *Red Prussiate of Potash* produces no precipitate: after some time, a slight opacity is visible, which disappears on the addition of muriatic acid.

Hydrosulphuret of Ammonia produces a red precipitate, which completely redissolves in an excess of the precipitant.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas,* produces in acid and neutral solutions of protoxide of antimony, a red precipitate. If the solution of protoxide of antimony is neutral, the sulphuretted hydrogen gas produces at first merely a red colour without a precipitate; but the latter is immediately produced, either by adding muriatic acid, or by exposing the solution to heat.

A bar of *Metallic Zinc* precipitates antimony from its solutions, in the metallic state, and in the form of a black powder.

The salts of protoxide of antimony cannot be heated to redness, in contact with the air, without being either decomposed or volatilized. Their solutions, which are always acid, redden litmus paper.

The compounds of protoxide of antimony which are insoluble in water, can be nearly all dissolved in muriatic acid. The presence of protoxide of antimony in the acid solution, is best detected by sulphuretted hydrogen gas. The acid with which the protoxide of antimony was originally combined, is then contained in the solution filtered from the sulphuret of antimony. If the insoluble compound consisted of protoxide of antimony in combination with a base instead of an acid, then the base exists in the filtered solution, in the state of chloride.

Before the *Blowpipe,* the salts of protoxide of antimony, when mingled with soda and heated in the inner flame, are reduced. The bead of metallic antimony thereby produced, remains long in the melted state after being removed from the flame, and gives off a thick white smoke. When the smoke ceases, the globule of antimony becomes covered with a network of crystals, which consist of protoxide of antimony. (BERZELIUS: *Ueber die Anwendung des Löthrohrs,* p. 81.)

Solutions of protoxide of antimony are most readily known by their behaviour with liquid sulphuretted hydrogen and hydrosulphuret of ammonia.

When the solution of protoxide of antimony contains non-volatile organic substances, it can very often be diluted with water, without being rendered milky. It is, on this account, that tartar emetic dissolves completely in water. From such a solution, however, if it be acid, red sulphuret of antimony can be precipitated by sulphuretted hydrogen gas. The presence of protoxide of antimony is, therefore, easy of detection.

XXX. OXIDE OF CHROMIUM.

Oxide of chromium in the state of hydrate is greyish-green, or when it has been strongly dried, green. It readily dissolves in acids, and the solution, even when very dilute, possesses a deep emerald-green colour; but if viewed by transmitted candle-light, it appears violet. The hydrate is deprived of its water by heat; and at the commencement of ignition, becomes strongly incandescent. The colour of the oxide is dark green. After ignition, it is insoluble in acids; it can, nevertheless, be dissolved, by being heated in sulphuric acid.

The solutions of oxide of chromium in acids, and those of the salts of oxide of chromium, in water, behave towards reagents as follows:

A solution of *Potash*, added in small quantity, produces a light green precipitate, which readily and completely redissolves, in the cold, in an excess of the precipitant. The colour of the resulting solution is green, possessing in general the same appearance as previous to the addition of the potash. If this solution is boiled, the green oxide of chromium is completely reprecipitated, and the supernatant solution becomes colourless. The colour of this precipitate is green, even by candle-light.

Ammonia produces in solutions of oxide of chromium, a greyish-blue precipitate, slightly tending towards violet. By candle-light, this precipitate appears of a perfect violet colour. The supernatant liquid possesses a reddish colour, and still retains in solution a trace of oxide of chromium, which can be precipitated by a prolonged digestion.

A solution of *Carbonate of Potash* produces in solutions of oxide of chromium, a light green precipitate, which on being allowed to repose for some time, becomes almost blue, and by candle-light, appears violet. An excess of the precipitant redissolves a considerable quantity of the precipitate, and thereby produces a solution, which, though at first green, becomes after some time bluish. A very great excess of the precipitant, redissolves the precipitated oxide completely. The resulting solution affords no precipitate when boiled.

A solution of *Bicarbonate of Potash* produces in the solution of oxide of chromium, a light green precipitate, and the supernatant liquid remains greenish. Upon being allowed to repose, both the precipitate and the solution become bluish. By candle-light, the precipitate appears violet.

A solution of *Carbonate of Ammonia* behaves in the same manner.

A solution of *Phosphate of Soda* produces in the neutral solution of oxide of chromium, a light green precipitate.

Solutions of *Oxalic Acid, Prussiate of Potash,* and *Red Prussiate of Potash,* produce no precipitate in solutions of oxide of chromium.

A solution of *Chromate of Potash* communicates to an acidulated solution of oxide of chromium, a deep brownish-yellow colour. The addition of ammonia to this solution produces a brownish-yellow precipitate, while the supernatant solution retains the same colour. The addition of a solution of chromate of potash to a neutral solution of oxide of chromium, immediately produces a yellow precipitate, while the supernatant solution acquires a brownish-yellow colour.

A solution of *Iodide of Potassium* produces in neutral solutions of oxide of chromium, a greenish-white precipitate, which is soluble in muriatic acid.

Hydrosulphuret of Ammonia produces in a neutral solution of oxide of chromium, a greenish precipitate of oxide of chromium.

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas,* produces no precipitate in acid or neutral solutions of oxide of chromium.

The neutral soluble salts of oxide of chromium redden litmus paper. The salts of oxide of chromium which are soluble in water, are decomposed by ignition.

The salts of oxide of chromium which are insoluble in water, are, previously to ignition, mostly soluble in acids. The solutions of these compounds very often behave in the same manner as acidulated solutions of pure oxide of chromium. In these cases, it is often easy to overlook the acid with which the oxide of chromium produces the compound which is insoluble in water. The presence of oxide of chromium in these compounds can very readily be detected by the blowpipe.

Before the *Blowpipe*, the compounds of chromium are very easily detected by the beautiful emerald-green colour which they communicate to the fluxes. The colour of the flux is equally green, both in the inner and outer flame, at least with microcosmic salt; the latter character distinguishes oxide of chromium from oxide of copper, which produces a green bead only in the outer flame. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 80.)

The compounds of oxide of chromium, can be distinguished with facility from most of the substances treated of in the preceding sections, by the examination of the smallest portions before the blowpipe. Solutions of oxide of chromium are characterised by their green colour. They are distinguished from the green solutions produced by other substances, by experiencing no alteration on being treated with liquid sulphuretted hydrogen.

The presence of non-volatile organic substances hinders the precipitation of oxide of chromium by alcalies.

B. ACIDS.

I. ACIDS OF SULPHUR.

a. SULPHURIC ACID.

In a pure and anhydrous state, sulphuric acid forms a tough stringy mass, which smokes very strongly in the air. This dry acid, however, can be very seldom presented for analysis. The hydrate of sulphuric acid is either fuming (Nordhausen oil of vitriol), in which case it can very easily be made to deposit crystals by a somewhat low temperature, or it is not fuming but of an oily consistence. The latter is its usual state, and is that of the commercial oil of vitriol. Both the fuming and the common oil of vitriol are perfectly colourless if pure; but the former is generally possessed of a brown colour, which is owing to the presence of an extremely small quantity of organic matter. The boiling point of sulphuric acid is far higher than that of water. It is not decomposed by boiling. It is a powerful decomposer of organic substances, and abstracts water from the air. When it is mixed with water or alcohol, it produces heat.

The acid and neutral sulphates are all soluble in water, excepting the compounds formed by sulphuric acid with barytes, strontian, protoxide of lead, and lime. These are partly very sparingly soluble, and partly quite insoluble in water; they are also insoluble in an excess of acid. The basic sulphates are nearly all insoluble in water, but soluble in diluted acids. The neutral sulphates are insoluble in strong alcohol, excepting the sulphates of peroxide of iron, of oxide of chromium, and of a few other bases which contain a considerable number of atoms of oxygen.

The presence of sulphuric acid, either in a free state, or in the salts which are soluble in water, is very easy of detection. Very dilute solutions, either of sulphuric acid or sulphates, produce, with the smallest quantity of a solution of a *barytic salt,* and that which answers the purpose best, in almost all cases, is a solution of chloride of barium, a white precipitate of sulphate of barytes. The addition of a free acid, for which experiment it is commonly best to choose muriatic acid, does not cause this precipitate to redissolve. It must be observed hereby, that when a salt for examination has been mingled with muriatic or nitric acid, and then tested with a concentrated solution of chloride of barium or of nitrate of barytes, a white precipitate of chloride of barium or of nitrate of barytes may be produced. This precipitate is sparingly soluble in free acids, but dissolves completely in water.

Solutions of *Protosalts of Lead* produce in solutions of sulphuric acid, or of the sulphates, a white precipitate, which is discriminated from similar white precipitates produced by protoxide of lead, by being insoluble in diluted nitric acid. Very small quantities of dissolved sulphates are, however, by no means so well detected by solutions of protosalts of lead as by solutions of barytic salts.

The aqueous solutions of sulphuric acid and of the sulphates, even when the latter have been mingled with a free acid, are not troubled by *Liquid Sulphuretted Hydrogen*, unless the acid be combined with a base which that reagent is capable of precipitating.

Basic sulphates, which are insoluble in water, must be dissolved in diluted muriatic acid. The solution must be diluted with water, and then tested with a solution of chloride of barium. The production of insoluble sulphate of barytes indicates the presence of sulphuric acid.

To detect the presence of sulphuric acid in the sulphates which are either insoluble or very sparingly soluble both in water and in acids, such as the sulphates of barytes, strontian, lime, and protoxide of lead, it is necessary to boil the compound in a solution of carbonate of potash or of soda. The solution is filtered from the undissolved residue, and after being supersaturated with muriatic acid, is mixed with a solution of chloride of barium. This immediately produces a white precipitate of sulphate of barytes, provided the insoluble substance contained sulphuric acid.

The sulphates of which the bases are alcalies, alcaline earths, or magnesia, are not decomposed by heat. The sulphates of which the base is protoxide of manganese, oxide of zinc, oxide of cobalt, oxide of nickel, oxide of cadmium, or deutoxide of copper are decomposed only by a very strong heat, and for the most part, or at least when the quantities are large, only very incompletely. The compounds of sulphuric acid with alumina, peroxide of iron, peroxide of tin, and even with protoxide of iron and protoxide of tin, are more easily decomposed when heated in contact with the air, and leave pure oxides. The compound of sulphuric acid with oxide of silver, leaves the pure metal on being ignited, and those containing protoxide and peroxide of mercury, leave no remainder.

Solutions of the neutral compounds of sulphuric acid with alcalies, lime, magnesia, and oxide of silver, leave the colour of blue litmus paper unchanged; but solutions of the neutral compounds of sulphuric acid with other bases, redden litmus paper.

Before the *Blowpipe,* sulphuric acid is detected in the sulphates, and especially in those which do not contain a metallic oxide, by the following experiment: A portion of the salt is added to a clear colourless bead formed by the fusion of soda with silica on charcoal, and the whole is heated in the inner flame. The colour of the bead is thereby rendered dark brown, or with small quantities, and when it is cold, red.—When a sulphate is melted with soda, on charcoal, in the inner flame, and the mass is taken from the charcoal, laid on a bright piece of silver, and moistened with water, the silver acquires a black or dark yellow stain. (BERZELIUS, *Anwendung des Löthrohrs,* p. 107.)

When the sulphates contain a metallic oxide as base, the presence of sulphuric acid is generally detected before the blowpipe, by the odour of sulphurous acid which is produced when the salt is ignited upon charcoal. But a safer process consists in heating a small portion of the salt on charcoal to expel the water of crystallisation, then pulverising it in a mortar, mixing it with a little charcoal powder, and afterwards heating the mixture by the blowpipe flame, in a little glass tube, closed at one end. A considerable quantity of sulphurous acid gas is then disengaged, and can not only be recognised by the smell, but also by its action on a strip of moistened Brazil-wood paper, which on being inserted into the upper part of the glass tube, becomes bleached.

The compounds formed by sulphuric acid with the earths and alcalies, do not disengage sulphurous acid, on being treated as above.

The behaviour of sulphuric acid and of the sulphates towards a solution of barytes, is so characteristic, that sulphuric acid cannot be mistaken for any other acid, except selenic acid. Solutions of the latter, when boiled with muriatic acid, disengage gaseous chlorine, which is not the case with solutions of sulphuric acid.

When organic substances are contained in a solution, it very often happens that at least a portion of the free sulphuric acid which it may contain, escapes precipitation by the solution of barytes. This is the case, for example, when a mixture of sulphuric acid and alcohol is the subject of experiment.

b. SULPHUROUS ACID.

Pure sulphurous acid is a gas, possessing a peculiar suffocating odour, by which it can be easily detected when present in the smallest quantities. By employing great cold and pressure, it can be converted into a colourless liquid. The gas bleaches moist Brazil-wood paper.

Sulphurous acid is soluble in water and in greater quantity in alcohol. The solutions possess the peculiar suffocating odour of the gaseous acid, and bleach Brazil-wood paper. When they have been exposed for some time to the air, the sulphurous acid is found to be either wholly or partly converted into sulphuric acid.

Solutions of sulphurous acid are deprived of their odour by a continued boiling, because the acid is volatilized. They are also deprived of their odour by being digested with brown oxide of lead, because the excess of oxygen of the base, oxidises the sulphurous acid, and occasions the formation of sulphate of protoxide of lead.

Solutions of the soluble sulphites do not smell of sulphurous acid when they are neutral, but they possess a peculiar taste. They are recognised by the odour of sulphurous acid which they disengage on being treated with muriatic, or, still better, with sulphuric acid. When the solution of the sulphite is very concentrated, the sulphurous acid is disengaged on the addition of the stronger acid, with effervescence. The residual liquid, when muriatic acid has been employed to decompose the salt, contains no sulphuric acid. No sulphur is separated when this decomposition is effected.—If the concentrated solution of a sulphite is mingled in the cold with nitric acid, sulphurous acid is disengaged; but if the mixture is boiled, yellow vapours of nitrous acid are disengaged, and sulphuric acid is formed in the solution.

Sulphurous acid is discovered in solutions by *Liquid Sulphuretted Hydrogen,* which produces a milky white precipitate of sulphur. If the solution contain a sulphite, the precipitation of sulphur does not take place, unless the operator adds diluted sulphuric or muriatic acid to the solution, either before or after the liquid sulphuretted hydrogen.

When solutions of sulphites are mixed with solutions of certain metallic salts, and a stronger acid, as, for example, muriatic acid, or diluted sulphuric acid, is added to the mixture, the metals are thereby reduced. From a solution of chloride of gold, metallic gold can thus be separated, even in the cold. A diluted solution of nitrate of silver which has been mingled with a solution of a sulphite and with diluted sulphuric acid, yields reduced silver, however, only when it is heated. The solution of a salt of deutoxide of copper, upon being boiled with a solution of an alcaline sulphite, yields protoxide of copper, which combines with the sulphurous acid and forms a voluminous light brown precipitate. Upon the addition of diluted sulphuric acid, this precipitate is decomposed. Sulphurous acid precipitates tellurium from a solution of chloride of tellurium, in the state of a black metallic powder. It also precipitates selenium from a solution of selenious acid; the precipitate has a cinnabar red colour and remains a long time suspended in the solution, but it contracts to a very small bulk upon being boiled, and at the same time acquires a black colour.

Sulphurous acid forms with alcalies, salts which are soluble in water. The compound which it produces with earths are insoluble in water, but soluble in acids. This is the reason that a solution of *Chloride of Barium* produces in neutral solutions of the sulphites a white precipitate, which fully redissolves in diluted muriatic acid. When the solution of a sulphite has been long exposed to the air, the precipitate produced by a solution of chloride of barium is no longer completely soluble in muriatic acid.—A solution of *Chloride of Calcium* also produces a precipitate which is soluble in muriatic acid.—A solution of a *Salt of Protoxide of Lead* produces also a precipitate, which completely dissolves in the cold in nitric acid; but if the mixture is boiled, yellow vapours of nitrous acid are disengaged, and insoluble sulphate of lead is produced.

In a solid form, the sulphites are known by the odour of sulphurous acid which they disengage, upon being moistened with an acid. When they are ignited in a glass tube closed at one end, they commonly first melt, and are then decomposed into a metallic sulphuret and a sulphate. If then the ignited mass is treated with a diluted acid, it disengages sulphuretted hydrogen gas, provided the metallic sulphuret be one of those which are able, with the assistance of a diluted acid, to decompose water.

Before the *Blowpipe*, the sulphites behave towards a bead of soda and silica, and, after fusion with soda on charcoal, towards silver, precisely in the same manner as the sulphates (page 154).

The sulphites can easily be detected by the characteristic odour of sulphurous acid which they produce on being treated with muriatic or diluted sulphuric acid. When this odour is perceived, and it is seen that no sulphur is precipitated, the sulphites cannot be mistaken for other substances.

II. ACIDS OF NITROGEN.

a. NITRIC ACID.

Nitric acid has never been obtained in an anhydrous state. It forms with water a colourless liquid, which at its state of greatest concentration, volatilizes at a temperature below the boiling point of water. When, on the contrary, it contains a greater quantity of water, in which state it is much more frequently employed, its boiling point rises as high as 248° Fahr., and in glass vessels even as high as 257° Fahr. The most concentrated acid is very easily decomposed: if submitted to distillation, it produces red vapours, and acquires a yellow colour. Upon being exposed to the light of the sun, and under various other circumstances, it becomes yellow, and the change in colour is accompanied by a disengagement of oxygen gas.

Diluted nitric acid, of the strength which is commonly found in commerce, is capable of oxidising most other substances. The greater part of the metals can be thereby converted into oxides. A portion of the nitric acid suffers decomposition in this case, and the products afforded, independent of the oxygen furnished to the metal, are partly nitrous acid, partly nitrous gas, and protoxide of nitrogen. Hence, whenever a metal is treated with nitric acid, reddish-yellow vapours are disengaged. This is the case, even with those metals whose solution in other acids is accompanied by the disengagement of hydrogen gas. The metallic oxides produced by this operation, are nearly all, with the exception of peroxide of tin and protoxide of antimony, dissolved by the undecomposed portion of the nitric acid. A few metals, platinum, rhodium, iridium, and gold, are not attacked by nitric acid. The most concentrated colourless nitric acid does not generally oxidise metals, excepting zinc.—Organic substances are also susceptible of oxidation by nitric acid. Most of them are converted by a prolonged digestion with the assistance of heat, into malic acid and oxalic acid. If the nitric acid is present in excess, it does not become coloured by this operation. A great number of organic substances, upon being treated with a smaller quantity of nitric acid than is necessary to effect their complete oxidation, acquire a characteristic yellow colour. This is the case with the skin of the human body, and with the corks which are employed to close the bottles which contain nitric acid.

The salts which nitric acid forms with bases, are nearly all easily soluble, so that nitric acid cannot be precipitated from its solutions, by solutions of any other salts. There are very few oxides which do not dissolve in it. These have been named above. Hence, the detection of nitric acid, when in a very dilute state, or when contained in solutions of nitrates of which the operator has very small portions for examination, is often more difficult than the detection of other acids.—When very small quantities of nitrates are in solution, it is best to evaporate the solution to dryness by a gentle heat, and to examine the salt in the dry state, by the following methods. When free nitric acid is contained in a solution, it is saturated with a base, for which it is best to take potash, and the nitrate is obtained in a dry state by the evaporation of the solution.

The methods of detecting nitric acid in solutions, are as follow:

To the solution of the nitrate, muriatic acid and a little pure *Gold-leaf* are added; the mixture is then heated, upon which the gold dissolves, and the solution becomes yellow. If the gold-leaf remain undissolved, there can be no nitric acid present.

The operator adds to the liquid, first a little sulphuric acid, and then a *Protosalt of Iron* in whole crystals, for which it is best to employ the protosulphate of iron. He then warms the mixture. If a nitrate is present, the liquid near the crystals acquires a dark blackish-brown colour, which is owing to the presence of dissolved nitrous gas. When the quantity of the nitrate is considerable, this colour is communicated to the whole solution. In very dilute solutions of nitrates, this dark colour is often imperceptible.

Small quantities of nitric acid and nitrates in solution, are detected by adding to the liquid, so much of a solution of indigo in sulphuric acid as is sufficient to render the whole distinctly but feebly bluish. To this solution, a little sulphuric acid is added, and the whole is boiled. The solution is then bleached, or when a very small quantity of nitric acid is present, it loses its blue colour, and becomes yellow. If a little chloride of sodium is added to the mixture before it is boiled, it is easy to detect the presence of $\frac{1}{500}$ of nitric acid. This reagent is recommended by LIEBIG. (POGGENDORFF'S Annalen, B. XIII. p. 200.)

The presence of nitric acid in the solid nitrates is detected by the following experiments:

Mingled with charcoal powder, and heated in a little porcelain crucible, they deflagrate and discharge sparks of fire. This is the most usual method of detecting the presence of nitric acid in the nitrates.

Mingled in a glass tube closed at one end, with *Copper Filings* and concentrated *Sulphuric Acid*, to which a very little water has been added, the nitrates, at the ordinary temperature, disengage orange-yellow vapours. When sulphuric acid, without copper filings, is added, the nitrates disengage colourless acid vapours, which form white clouds when a glass rod moistened with ammonia is held over the surface of the mixture.

Metallic Zinc is dissolved in *Mercury*, in such a proportion that the fluidity of the mercury is only slightly diminished. A portion of this amalgam is placed in a little porcelain capsule, and is barely covered with a neutral solution of *Protochloride of Iron*. A small piece of a nitrate is then laid upon the mercury in the solution, and after some time, a black stain is produced upon the mercury, just at the spot where the nitrate has been placed. By this process, which has been given by RUNGE (POGGENDORFF'S Annalen, B. IX. p. 479), the smallest portion of a solid nitrate can be detected.—Solutions which contain nitric acid or nitrates, also produce black stains on various parts of the amalgam, but not so distinctly as the solid salts.

The nitrates are all decomposed by ignition. Some of them, on being exposed to heat, first disengage oxygen gas, and are converted into nitrites, which are also decomposed by a stronger heat. Other nitrates, particularly such as contain metallic oxides as bases, give out both oxygen gas and nitrous acid on being ignited. If, therefore, these nitrates are heated over a spirit lamp in a white glass tube closed at one end, the glass tube becomes filled with yellow vapours, so that the presence of nitric acid can readily be detected by this experiment. A very few nitrates yield, on ignition, their nitric acid in an undecomposed state, in company with their water of crystallisation. Nitrate of ammonia is converted, by heat, into pure water and protoxide of nitrogen.

Of the preceding experiments, those in which the nitric acid in the nitrates is detected by means of copper filings and sulphuric acid, or by sulphuric acid and a protosalt of iron, give the most decisive results. The phenomena which occur in the other experiments, can also be produced by the reaction of substances which do not contain nitric acid.

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b. NITROUS ACID.

Nitrous acid in a pure state, and when exposed to a very low temperature, is a liquid possessing a deep green colour. This liquid, on being exposed to a still lower temperature, becomes colourless. It is very volatile; at the usual temperature of the atmosphere, it forms a dark yellowish-red gas. It is never presented in a pure state for analytical examination; but the compound which it forms with nitric acid, is more frequently the subject of experiment. This compound is held, by some chemists, to be a peculiar oxide of nitrogen, and is termed nitrous acid, while the true nitrous acid receives from the same chemists, the name of hyponitrous acid.

Nitrous acid dissolves in water, yet not without experiencing a partial decomposition. The solution is accompanied by a disengagement of nitrous gas, and the liquid contains a compound of nitric acid, nitrous acid, and water.

The compounds of nitrous acid with bases cannot be produced by the direct combination of their constituents. They very much resemble the nitrates, and, like the latter, are characterised by deflagrating on being mixed and heated with charcoal powder. It is possible, however, to distinguish them with accuracy from the nitrates, by the experiments which follow:

When the solution of a nitrite is mingled with muriatic acid and a portion of *Gold-leaf*, and the mixture is heated, the gold does not dissolve, provided no nitrate be present. When the solution is concentrated, it becomes slightly yellowish, but this colour is not attributable to the presence of dissolved gold; for, when the solution is diluted with water, the colour disappears.

When solutions of the nitrites are submitted to distillation, a slow boiling expels nitrous gas which on passing into the air produces yellowish-red vapours of nitrous acid, and in the meantime the salt in solution is converted into a nitrate. When solutions of the nitrites are boiled in the open air, they are easily converted into solutions of nitrates.

When nitrites, in a solid state, are treated with *Sulphuric Acid*, in the cold, in a white glass tube closed at one end, they disengage yellowish-red vapours of nitrous acid.

Ignition converts some of the nitrites, those, for example, which contain alcalies, into compounds which contain alcalies in combination with nitrous gas.

The nitrites can probably be mistaken for no other compounds than nitrates, and they can be distinguished from these, by the properties cited above.

The *Compound of Nitrous Acid with Nitric Acid*, which, as above stated, is considered by some chemists to be a peculiar acid, is contained in the fuming nitric acid. This acid, according to MITSCHERLICH (POGGENDORFF'S *Annalen*, B. XV. p. 618), consists of a solution of nitrous-nitric acid in nitric acid. It is almost wholly decomposed by water, which converts the nitrous acid into nitric acid, while nitrous gas is disengaged. The fuming nitric acid, however, invariably retains a portion of nitrous acid, even after dilution with water. When the fuming nitric acid has been diluted with water, it is deprived of its peculiar yellowish red colour, and becomes colourless.

III. CHLORIC ACID.

The hydrate of chloric acid is a colourless liquid, which can be reduced by gentle evaporation to the consistence of an oil. It can be volatilized, but a small portion is decomposed during the volatilization, into oxygen gas and peroxide of chlorine. Chloric acid, like most other acids, dissolves zinc and iron under disengagement of hydrogen gas. It experiences scarcely the least alteration on exposure to atmospheric air, and is even very slightly affected by exposure to the light of the sun. It reddens litmus paper, but the reddened paper, on being allowed to remain untouched, becomes bleached, in consequence of the decomposition of the acid. Chloric acid converts sulphurous acid into sulphuric acid, and is at the same time reduced to chlorine. It converts sulphuretted hydrogen gas into sulphuric acid, sulphur, and water, and muriatic acid into chlorine and water. It is distinguished by the latter characters from perchloric acid, which is not decomposed by these compounds.

Chloric acid produces with bases compounds which are much more frequently the subject of chemical examination than the acid itself is, for the chlorates are applied to technical purposes. They are mostly easily soluble in water, and only a few of them, as, for example, the chlorate of potash, are difficult of solution. On this account, chloric acid cannot be precipitated from solutions of the chlorates, either by a base or by solutions of other salts. Hence, solutions of pure chlorates produce no precipitate with a solution of nitrate of silver; but as the chlorates which have not been prepared by the saturation of pure chloric acid with bases, are very frequently contaminated by metallic chlorides, from which it is often difficult to separate them, it commonly happens that their solutions become troubled by a solution of nitrate of silver.—Solutions of pure chlorates exert no action on litmus, which can be attributed to the acid.

When dry chlorates are ignited, they disengage oxygen gas and are converted into metallic chlorides. To prove this by experiment, it is only necessary to heat a small quantity of a chlorate over the spirit lamp, in a little glass tube closed at one end, and to hold a glimmering splinter of wood to the mouth of the tube; upon which, the oxygen gas which streams out of the tube causes the wood to inflame and to burn with vigour. If the ignited residue is then dissolved in water, the resulting solution affords with a solution of nitrate of silver, a dense precipitate of chloride of silver.

When concentrated *Sulphuric Acid* is poured in the cold over chlorates contained in an open vessel, as, for example, in a rather wide glass tube closed at one end, vapours of peroxide of chlorine are disengaged. This gas is known by its greenish yellow colour, which is nearly the same as the colour of chlorine gas, but much stronger. In performing this experiment, it is necessary to employ but a small quantity of the salt, and to avoid the application of heat, otherwise an explosion will take place.—When the chlorates are mixed with a little diluted *Muriatic Acid* and cautiously warmed, they disengage greenish yellow vapours of protoxide of chlorine.

When the chlorates, particularly such as contain no water of crystallisation, are heated in company with sulphur, charcoal, or carbonaceous substances such as sugar, with certain metals and metallic sulphurets, and particularly with phosphorus, they explode with great violence. It is therefore necessary to be very cautious in performing these experiments, and to operate with very small quantities. When the chlorate is mixed with sulphur or cinnabar, or more especially with phosphorus, the mixture can even be made to explode, by being struck with a hammer upon an anvil. It also explodes on being pounded in a metallic mortar.—If a mixture of a chlorate with sulphur is moistened with fuming sulphuric acid, it bursts into a flame. When common oil of vitriol is employed in this experiment, it does not always produce a flame, though it invariably gives rise to a very violent action. In both cases, the odour of chloride of sulphur is produced.

By the violent explosion produced by heating the chlorates with combustible bodies, and by the yellowish green, and not yellowish red gas, disengaged by treating them with sulphuric acid, they can be readily recognised, and are moreover distinguishable by the latter property from the nitrates and nitrites.

IV. BROMIC ACID.

Bromic acid, in combination with water, is a colourless liquid, which, like the hydrate of chloric acid, is capable of being evaporated to the consistence of a syrup. It cannot, however, be distilled, without being partially decomposed into bromine and oxygen gas. It reddens litmus paper, but when the litmus paper remains for some time in contact with the acid, it becomes bleached. Muriatic acid, hydrobromic acid, sulphurous acid, and sulphuretted hydrogen decompose bromic acid in the same manner as they decompose chloric acid.

Some of the bases which produce soluble salts with chloric acid, produce with bromic acid compounds which are either insoluble, or very sparingly soluble. Solutions of bromates produce, for example, a white precipitate with a solution of *Nitrate of Silver*, even when the bromates are totally free from metallic bromides. This precipitate is soluble in ammonia, and insoluble in diluted nitric acid. It is, however, distinguished from chloride of silver by being only very slightly blackened on exposure to the action of light, and, like all the bromates, by causing an explosion, on being mingled and heated with charcoal.

A concentrated solution of *Nitrate of Lead* produces in concentrated solutions of bromates a white precipitate, which redissolves when the solution is diluted with water.

The solid bromates, like the solid chlorates, are decomposed by ignition: Oxygen gas is expelled, and metallic bromides are produced. They explode with nearly the same degree of violence as the chlorates, on being mingled and heated with sulphur, charcoal, or other combustible bodies; these mixtures can also be caused to explode by a blow; and they are likewise inflamed by being moistened by fuming sulphuric acid. When the bromate contains water of crystallisation, these phenomena are produced in a less striking manner. When bromates are mingled, in the cold, with concentrated sulphuric acid, in a glass tube closed at one end, they disengage bromine gas, which is easily recognised by its hyacinth red colour. At the same time, oxygen gas is also liberated. Most of the bromates are decomposed, if dissolved in a very small quantity of water, mixed with sulphuric acid or nitric acid, and then exposed to heat. The whole solution then acquires a beautiful hyacinth red colour, in consequence of the presence of free bromine. Many bromates, as, for example, the bromate of barytes, cannot be decomposed in this manner when in solution, but their decomposition is effected, when the acid is heated with the dry bromate.

The bromates have most similarity with the chlorates. Their solutions are distinguished from those of the latter, by giving a white precipitate with a solution of nitrate of silver. The dry salts are distinguished by producing in the cold with concentrated sulphuric acid, not a yellowish green gas, but a hyacinth-red gas, of a colour similar to that of nitrous acid. The bromates are distinguished from the nitrites, by the difference in the mode of their decomposition when ignited. They are distinguished from other salts, by producing an explosion on being mingled and heated with combustible bodies.

V. IODIC ACID.

The hydrate of iodic acid, can, according to SERULLAS (POGGENDORFF's Annalen, B. XVIII. p. 112), be obtained in a crystallised state. It easily dissolves in water, but is only slightly soluble in alcohol. It experiences no change on exposure to the air. It possesses a peculiar odour.

The aqueous solution of iodic acid, first reddens litmus paper, and after some time, bleaches it. Sulphurous acid, muriatic acid, and sulphuretted hydrogen gas, decompose it in the same manner as they decompose chloric acid (page 163).

Most of the compounds formed by iodic acid with bases, are either insoluble or but sparingly soluble, excepting the iodates of alcalies.

Sulphuric acid and other oxygen acids appear to affect the iodates in no other manner, than partly to convert them into acid iodates, and partly to separate the iodic acid.

When the iodates are mingled and heated with combustible bodies, they detonate like the chlorates and bromates, but much less forcibly.

When the iodates are ignited in a little retort, they disengage oxygen gas, and are converted into metallic iodides. When acid iodates are treated in this manner, they not only disengage oxygen gas, but also violet-coloured vapours of iodine. The fixed result is still a metallic iodide.

The iodates are best and most safely recognised, from the production of oxygen gas and metallic iodides when they are ignited in a little retort. The disengagement of oxygen gas is very easily discovered by holding a glimmering splinter of wood at the mouth of the retort during the ignition. The combustion of the wood then proceeds with unusual vigour. The methods of recognising the metallic iodides, or rather the iodine in the metallic iodides, will be indicated farther on, under the head of metallic iodides.

VI. PHOSPHORIC ACID.

Anhydrous phosphoric acid can be obtained by burning phosphorus in a large quantity of oxygen gas; it appears in the form of white flocks. The hydrate of phosphoric acid is obtained in the solid state, by evaporating the aqueous solution in vessels of platinum, heating the residue for a considerable time over a gentle fire in a covered platinum crucible, and finally exposing it to ignition. The resulting solid hydrate of phosphoric acid is a glassy mass, which becomes moist in the air and deliquesces to a liquid of the consistence of syrup. If the ignited mass, upon becoming cool, is treated with water, it completely dissolves, and the dissolution is accompanied by a crackling, which continues for some time. When the phosphoric acid has not been heated in the covered platinum crucible for a sufficient length of time, it produces a glutinous mass on cooling. When phosphoric acid of the consistence of syrup is heated in an open platinum vessel, it volatilizes in the form of a dense white smoke, and if it be perfectly pure, and the heat is sustained, it leaves no residue. The more impure the phosphoric acid, the less volatile is it, and the less liable to deliquesce on being cooled in the open air. When, therefore, a phosphoric acid affords no smoke on being ignited in an open vessel of platinum, and produces a glass which is not deliquescent in the air, and which is but sparingly soluble, or even quite insoluble, in water, the phosphoric acid is contaminated by a considerable quantity of fixed constituents, and the glass is then free from water.

Phosphoric acid strongly attacks vessels of glass or porcelain, when it is fused therein. The acid is thus rendered less deliquescent and less volatile, and no longer dissolves completely in water.—Pure phosphoric acid is easily soluble in water and in alcohol.

Of the salts which phosphoric acid forms with bases, none, in a neutral state, are soluble in water, excepting those which contain an alcali. The neutral compounds of phosphoric acid with the earths and metallic oxides are insoluble in water, and can only be dissolved by an excess of phosphoric acid, or of some other free acid. After ignition, however, many of the acid phosphates are insoluble in most acids, and can only be dissolved by being boiled with concentrated sulphuric acid. They cannot be dissolved even by that operation, if they contain a base which produces an insoluble compound with sulphuric acid.—The neutral solutions of the phosphates of alcalies, afford precipitates with the neutral solutions of the salts of all earths and metallic oxides. These precipitates are soluble in free acids, and are capable of reprecipitation in the state of phosphates, by the saturation of the acid with an alcali. But an excess of the alcali, particularly an excess of potash, often deprives the salt of its phosphoric acid, and the oxide then appears with its characteristic colour: it is not possible, however, to deprive the precipitate of the whole of its phosphoric acid by a process of this description. When the bases of the precipitated phosphates are soluble in an excess of the alcali, so is also the phosphate itself. In this respect, phosphoric acid has great similarity with other acids which produce with alcalies salts which are soluble in water, and with earths and metallic oxides, salts which are insoluble in water.

Solutions of the neutral phosphates of alcalies, therefore, not only produce precipitates with solutions of *Chloride of Barium*, *Chloride of Calcium*, and other soluble earthy salts, but also with *Lime Water* and *Barytes Water*. These precipitates are soluble in muriatic and nitric acids; they are also dissolved by solutions of ammoniacal salts, especially of muriate of ammonia. The precipitated phosphate of lime is particularly soluble in these solutions. A considerable quantity of the ammoniacal salt is nevertheless required to effect the perfect solution of the precipitate, and even when the solution is effected, the addition of free ammonia is sufficient to reprecipitate nearly the whole of the phosphate from the solution. When also phosphate of lime or of barytes is dissolved in a free acid, it can be precipitated from the solution by ammonia.

The white precipitate which is produced in solutions of phosphates of alcalies by a solution of *Acetate* or *Nitrate*

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The white precipitate which is produced in solutions of phosphates of alcalies by a solution of *Acetate* or *Nitrate* *of Lead*, is almost insoluble in free acetic acid, but is dissolved by nitric acid. If this precipitate of phosphate of lead is dried, and then fused upon charcoal, in the outer flame of the blowpipe, the fused lead becomes distinctly crystalline upon cooling. (BERZELIUS: *Anwendung des Löthrohrs.*)

A solution of *Nitrate of Silver* produces a yellow precipitate in solutions of the neutral phosphates of alcalies. This, of all the precipitates which are produced by phosphoric acid, is that by which the acid is best characterised; for all the other acids which have much resemblance to phosphoric acid, produce with oxide of silver, precipitates which possess a different colour, with the single exception of arsenious acid.—Even when the solutions, both of the phosphate and the salt of silver, were neutral, the liquid which is left above the yellow precipitate reddens the blue litmus paper, because the precipitate is a basic salt. It is only in a solution of phosphate of soda, recently prepared from a salt which has shortly before been strongly ignited, that the solution of nitrate of silver produces a white precipitate of neutral phosphate of silver.—The yellow precipitate of phosphate of silver is soluble both in nitric acid and in ammonia; and indeed is not insoluble in a liquid which contains nitrate of ammonia. When, therefore, a solution containing a small quantity of phosphate of silver, in a large quantity of nitric acid, is cautiously saturated with ammonia, no precipitate is produced.

Phosphoric acid, contained in neutral and acid compounds which are soluble in water, is neither precipitated nor converted into a lower oxide of phosphorus, by sulphuretted hydrogen gas, by sulphurous acid, nor by any other reagent.

The presence of phosphoric acid, in the phosphates which are insoluble in water, can sometimes be easily overlooked, particularly when the compounds contain a great number of constituents, and when other acids are present which behave towards reagents in the same manner as phosphoric acid. Very considerable caution is required in this case, to avoid overlooking even a large quantity of phosphoric acid.

When the phosphoric acid is combined with barytes, strontian, lime, or magnesia, the presence of phosphoric acid is detected, if the compound dissolves in muriatic acid and can be again thrown down as a white precipitate, by supersaturating the acid solution with ammonia. But the operator must have previously convinced himself, by means of other experiments, that neither arsenic acid, boracic acid, fluorine, nor certain organic acids, form part of the substance under examination; for barytes, strontian, and lime can only be precipitated from solution by ammonia, when they are combined with phosphoric acid, arsenic acid, boracic acid, or some organic acids, or when their metals are combined with fluorine. And magnesia also, which cannot be precipitated by ammonia from solutions which contain muriate of ammonia or other ammoniacal salts, is nevertheless precipitated by ammonia, when phosphoric acid is present.

A more difficult thing, however, is to detect the presence of phosphoric acid when it is combined with alumina. The phosphate of alumina behaves towards most reagents exactly like pure alumina: the acid solution is precipitated in the same manner by ammonia, and the precipitated phosphate of alumina is equally soluble with pure alumina in an excess of pure potash and in free acids. To detect the presence of phosphoric acid in the phosphate of alumina, the salt is first dissolved in muriatic acid, and the solution is mingled with so much of a solution of pure potash, that the precipitate of phosphate of alumina which first appears, is again completely redissolved. To this solution, a solution of silicic acid in potash (silicated potash, liquor of flints) is next added. The alumina is thereupon precipitated in combination with silicic acid and potash, in the state of an insoluble gelatinous mass, either immediately, or after some time. The solution is filtered from this precipitate, and mingled with a solution of chloride of calcium, whereupon, if phosphoric acid be present, a precipitate of phosphate of lime appears. But it is better to add a very slight excess of muriatic acid to the alcaline solution, particularly when the potash is likely to contain carbonic acid, and then to saturate the acid with a little ammonia, and to precipitate the solution by chloride of calcium.

When the phosphoric acid is combined with metallic oxides which are capable of being precipitated by hydrosulphuret of ammonia from a solution which has previously been saturated or supersaturated with ammonia, but which are incapable of precipitation from acid solutions by sulphuretted hydrogen gas, and which oxides are consequently those of manganese, iron, zinc, cobalt, nickel, and uranium, then the operator must precipitate these substances, in the state of metallic sulphurets, by hydrosulphuret of ammonia. The solution, filtered from the resulting metallic sulphuret, is slightly acidulated by muriatic acid, and allowed to digest in a warm place, until it has no longer the odour of sulphuretted hydrogen. The solution is filtered from the precipitated sulphur, and saturated with ammonia. It is better, however, to add to the filtered solution, such a quantity of carbonate of potash as leaves the acid still slightly in excess, so that it can distinctly redden litmus paper. The vessel should then be placed for some time in a warm situation, to facilitate the expulsion of the carbonic acid, which must be separated as completely as possible. A sufficient quantity of ammonia is then to be added to the solution to redden it capable of effecting a slight change in the colour of reddened litmus paper. To the solution thus prepared, a solution of chloride of barium, or, still better, of chloride of calcium, is added, upon which, if phosphoric acid is present, and arsenic acid, boracic acid, fluorine, and organic acids are absent, a precipitate of phosphate of barytes or of lime is produced.—The saturation of the acid solution by carbonate of potash is preferable to the saturation by ammonia, because the phosphates of lime and barytes, as has been observed above, are partially soluble in solutions which contain ammoniacal salts. When a very small quantity of a phosphate is submitted to examination, and the solution has been saturated by ammonia alone, it sometimes happens that the addition of a solution of chloride of barium, or chloride of calcium, produces no precipitate of phosphate of barytes or phosphate of lime, because the entire quantity is dissolved by the ammoniacal solution.

When the phosphoric acid is combined with a metallic oxide which can be precipitated from an acidulated solution by sulphuretted hydrogen gas, the operator employs this reagent to precipitate the metal in the state of sulphuret. The solution filtered from the metallic sulphuret is exposed to heat, for the purpose of expelling the excess of sulphuretted hydrogen. It is then examined for phosphoric acid, in the manner which is described above.

When the phosphoric acid is combined with a metallic oxide which is capable of precipitation in the state of sulphuret, neither from an acidulated solution by sulphuretted hydrogen gas, nor from an ammoniacal or neutral solution by hydrosulphuret of ammonia, but which is insoluble in a solution of potash, then the best method of proceeding is as follows: The phosphate is dissolved in the smallest possible quantity of an acid, and the solution is boiled with an excess of a solution of potash. The phosphate is thus deprived of the greater part of its phosphoric acid, and the metallic oxide is precipitated, usually with the colour which characterises it when pure. The precipitate, however, contains a small quantity of phosphoric acid, though the greater part of the phosphoric acid, exists, in combination with potash, in the filtered solution. A sufficient quantity of muriatic acid is added to the latter, to saturate the potash and to render the solution slightly acid. It is then mixed with a solution of chloride of calcium, together with a little ammonia to saturate the free acid. This produces a precipitate of phosphate of lime. Acids which behave towards reagents in the same manner as phosphoric acid, can also be separated from their bases by potash and be made to afford a precipitate with a solution of chloride of calcium, exactly in the same manner as phosphoric acid. The operator must therefore convince himself that the compound for examination is free from these acids, before he can determine with certainty that the precipitate produced in the above operation, by a solution of chloride of calcium, actually consists of phosphate of lime. The presence of phosphoric acid can be detected by the above process, when it is combined with oxide of chromium and protoxide of cerium. It can also be often more easily detected in this than in any other manner, when it exists in combination with magnesia, protoxide of manganese, the oxides of iron, and some other bases.

To detect phosphoric acid in extremely small portions of phosphates, it is best, according to THENARD and VAUQUELIN, to proceed as follows: A portion of metallic potassium or sodium is placed at the bottom of a small glass tube closed at one end, and the phosphate for examination is placed upon the metal. The phosphate must be perfectly dry, but need not be in greater quantity than the $\frac{1}{150}$ of a grain. The whole is then cautiously heated to ignition, upon which the potassium or sodium reduces the phosphoric acid to phosphuret of potassium or phosphuret of sodium. The excess of potassium or sodium is removed by means of a small portion of mercury, which is poured into the little glass tube and soon poured out again. The operator then cautiously blows through a fine tube, upon the mass contained in the glass tube, with a view to moisten it. The mass is thus made to smell strongly and characteristically of phosphuretted hydrogen gas.

Before the *Blowpipe*, phosphoric acid, in the solid phosphates, cannot be detected without difficulty. According to BERZELIUS, the operator should proceed as follows: A portion of the compound for examination is fused with boracic acid on charcoal, and when the intumescence is ended, a piece of fine iron harpsichord wire is thrust into the bead in such a manner that the two ends of the wire project out of the bead; the whole is then strongly heated in the inner flame. The resulting bead is, when cold, taken from the charcoal, wrapped in a piece of paper, and crushed in two, by a slight blow from a hammer. The operator then finds a round grain of phosphuret of iron, which possesses a metallic appearance, is magnetic, and brittle, so that it springs to pieces when struck with a hard blow. The presence of a small quantity of phosphoric acid in the substance submitted to examination, cannot be detected by this operation. The assay must contain no sulphuric acid, arsenic acid, nor any metallic oxides which can be reduced by iron; for otherwise the experiment will produce globules agreeing in brittleness, fusibility, and many other particulars, with the phosphuret of iron. This method, moreover, requires considerable address in the operator. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 111.)

If a solid phosphate is moistened with sulphuric acid and held by the platinum forceps, in ~~the inner~~ flame of the blowpipe, it communicates a green colour to the outer flame. This method of detecting phosphoric acid before the blowpipe, is given by FUCHS (SCHWEIGGER'S Journal, B. XXIV. p. 130). It is only in some cases, however, that it affords a good result; and it must be borne in mind, that borates produce the same effect.

The phosphates are not volatilized by heat, when the phosphoric acid is combined with fixed bases. The greater part of these are fusible at a high temperature, particularly the acid phosphates; but the phosphates which have been fused are insoluble in most acids. A great number of phosphates are decomposed by being ignited with charcoal; in many cases, metallic phosphurets are then formed, while in other cases, particularly when an excess of phosphoric acid is present, phosphorus is sublimed.

From what has been said on the behaviour of phosphoric acid towards reagents, it is easy to perceive that the detection of that acid is very frequently accompanied by considerable difficulties. The presence of phosphoric acid can only be determined with certainty, when the operator has convinced himself by previous experiments, that the substances for examination contain none of the other acids, whose reactions are similar to those of phosphoric acid. There is only one property, which is characteristic of phosphoric acid alone; it is, that when combined with protoxide of lead, it forms a salt which, after being fused before the blowpipe, crystallizes as it cools. The phenomena produced with metallic potassium are also peculiar to phosphoric acid and the phosphates. By these alone, therefore, can it be distinguished from all other sub-

VII. BORACIC ACID.

Boracic acid, in a state of purity, forms a colourless, transparent and brittle glass, which fuses at a red heat, and is not volatile. After being fused in a platinum vessel, it dissolves in water with some difficulty. If it is dissolved in hot water, the solution, on cooling, deposits crystalline scales of hydrate of boracic acid. These crystals have a splendour resembling that of mother-of-pearl, and are greasy to the touch. They dissolve sparingly in water. The solution changes the colour of blue litmus paper to red, but at the same time, it renders turmeric paper brown, in which respect it acts like an alcaline solution. When the aqueous solution of boracic acid is slowly evaporated, a considerable quantity of the acid is volatilized with the water. Boracic acid is also soluble in alcohol, to the flame of which it has the property of communicating a green colour. This is most distinctly observable when the solution is stirred, or when the alcohol is nearly all consumed. This colouring of the flame of burning alcohol is the property which is most characteristic of boracic acid. If the spirituous solution of boracic acid is submitted to evaporation, a very considerable quantity of the acid is volatilized with the spirit.

Of the salts of boracic acid, those only which have an alcali as base, are capable of solution in water. The compounds of boracic acid with the earths and metallic oxides, are in a neutral state, either quite insoluble, or but sparingly soluble, in water. When neutral solutions of alcaline borates are mixed with neutral solutions of salts which contain earths or metallic oxides, precipitates are produced if the solutions are not too dilute. Thus, for example, precipitates are produced when neutral solutions of borates are mixed with a concentrated solution of *Chloride of Barium*. The resulting precipitate is completely soluble in a large quantity of water, and still more easily soluble in a solution of muriate of ammonia. The precipitate, produced in solutions of borates, by a solution of *Chloride of Calcium*, is still more soluble in water, and particularly in a solution of muriate of ammonia, than even the borate of barytes. Far more difficult of solution, however, are the precipitates which are produced in solutions of the borates, by solutions of *Nitrate of Lead*, *Protonitrate of Mercury*, and *Nitrate of Silver*. The precipitate produced by nitrate of lead is white; that produced by protonitrate of mercury is brown; that produced by nitrate of silver, is white when thrown down from concentrated solutions of borates, but brown when precipitated from diluted solutions. Both of these precipitates are easily soluble, either in ammonia or in diluted nitric acid.

When soluble borates are boiled with diluted sulphuric acid, they are decomposed; and as the solution becomes cool, it deposits crystalline scales of the sparingly soluble hydrate of boracic acid. The crystals are readily recognised to be those of boracic acid, by the properties which are described above. Before they are submitted to any experiment, they must be purified, by washing with water, from the free sulphuric acid and soluble sulphates which adhere to them.

Boracic acid, in the borates, is detected as follows: The borate is pulverised, placed in a porcelain capsule on a platinum crucible, moistened with some drops of sulphuric acid, and covered with alcohol, which is then inflamed. The flame produced by the burning alcohol has a green colour, which is most observable when the mixture is stirred. It is necessary that the salt under examination contain no chloride; because chlorides, of themselves, when moistened with sulphuric acid, communicate to the flame of burning alcohol a greenish colour, in consequence of the formation of muriatic ether. Yet in this case, the colour of the flame is bluish green, and has very little similarity to that which indicates the presence of boracic acid.

According to TURNER, the borates can be detected before the blowpipe as follows: The salt is mixed with a flux composed of one part of pulverised fluor spar and four and a half parts of bisulphate of potash. The mixture, moistened with a little water, is held on a platinum wire, and exposed to the point of the inner blowpipe flame.

Shortly after the fusion, there appears a green colour around the flame, which soon disappears, however, and is not again seen. (BERZELIUS: *Anwendung des Löthrohrs*, p. 113.)

The most decisive indication of the presence of boracic acid, is the green colour communicated to the flame of burning alcohol, either by free boracic acid, or by a mixture of borates with sulphuric acid.

VIII. CARBONIC ACID.

Carbonic acid in a pure state, is a colourless gas, which is incombustible itself, and incapable of supporting the combustion of other bodies. It is also unfit for respiration. Carbonic acid gas is heavier than atmospheric air, so that it can be poured from one vessel into another, nearly as accurately as a liquid; nevertheless, like all other gases, it mingles pretty quickly with atmospheric air. Moistened blue litmus paper is reddened by carbonic acid gas, but the red colour disappears when the paper is exposed to the air. Carbonic acid dissolves in water; but when the solution is exposed for some time to the air, or when it is boiled, the carbonic acid escapes almost completely. The solution of carbonic acid in water reddens blue litmus paper like the gaseous acid, and the red colour is equally fleeting. *Lime Water*, *Barytes Water*, and *Strontian Water*, produce white precipitates in the solution of carbonic acid. When, however, but a small quantity of lime water is added to the solution, the precipitate dissolves when the liquid is stirred: the precipitate also dissolves, even when present in larger quantity, if carbonic acid water is added in excess.

Of the salts produced by carbonic acid, all which contain alcalies for bases, whether they be acid or neutral, are soluble in water. The compounds formed by carbonic acid with earths and metallic oxides are, when in a neutral state, insoluble in water. On this account, solutions of salts of the earths and metallic oxides, are precipitated by solutions of the carbonates of alcalies. If, in these decompositions, the carbonic acid cannot combine with the base, it escapes in the gaseous form, with the production of effervescence, and the base precipitates in a free state; this is the case when neutral salts of alumina are precipitated by carbonates of alcalies. Solutions of the carbonates of alcalies are not only precipitated by the salts of the earths, but also, in some cases, by the earths themselves; thus, for example, precipitates are produced by *Lime Water*, *Barytes Water*, and *Strontian Water*.—A very small number of the carbonates which are insoluble in water, are easily soluble in a solution of carbonic acid in water. One of the most remarkable of these substances, is the carbonate of magnesia. Hence, the neutral solutions of the salts of magnesia, afford a precipitate with a solution of carbonate of potash, but none with a solution of bicarbonate of potash.

The aqueous solutions of the carbonates, are decomposable by all the acids which are soluble in water, and the carbonic acid is expelled in the state of gas, which, in escaping, produces effervescence. When the quantity of the carbonate is too small, the decomposition is not accompanied by effervescence, because the free carbonic acid is dissolved by the water. When also the quantity of the carbonate is greater, or even when it is present in very considerable quantity, the addition of the first portion of acid produces an extremely slight effervescence, which in many cases is totally unobservable. The reason of this is, that the carbonic acid which is expelled from one portion of the carbonate, combines with the remaining portion and produces a bicarbonate. The operator must therefore continue to add the acid gradually to the solution of the carbonate, until the decomposition of the latter is completely effected. It is then found that the effervescence produced by the discharge of the carbonic acid gas, becomes gradually stronger in proportion as the decomposition advances. When, on the contrary, a small quantity of the solution of the carbonate is poured into the solution of the acid, a strong effervescence is at once produced.

All the carbonates which are insoluble in water are decomposed, under disengagement of carbonic acid gas, when treated in a pulverised state, with a free acid. When the base of the carbonate, and the acid which is employed to decompose the carbonate, are capable of forming a soluble compound, the carbonate is completely dissolved by the acid. When the carbonic acid has been entirely expelled, the supersaturation of the acid solution by ammonia, cannot effect the precipitation of the insoluble carbonate; but it can nevertheless produce a precipitate, if the base is one of those whose soluble salts are precipitable by ammonia. This precipitate, however, can consist only of the base, without any proportion of acid. By this circumstance, the precipitates produced by alcaline carbonates, are distinguished from those which are produced by all other alcaline salts whose acids, like carbonic acid, produce insoluble compounds with earths and metallic oxides. When, for example, a solution of carbonate of potash or of soda is added to a solution of chloride of barium, of chloride of calcium, or of any other soluble salts of barytes or lime, and the resulting precipitate is dissolved in muriatic acid, the supersaturation of the acid solution with ammonia does not reproduce the same precipitate. But if, instead of carbonate of alcali, the operator employs phosphate of alcali, to precipitate the barytic or calcareous solution, then the precipitate produced by supersaturating the muriatic acid solution of the first precipitate, with ammonia, is the identical phosphate of lime or barytes which was dissolved in the muriatic acid.

The effervescence, which accompanies the decomposition of the carbonates, is not accompanied by any very characteristic odour. If they are decomposed by diluted sulphuric acid, and a glass rod, moistened with ammonia, is held over the vessel, scarcely any white clouds can be observed. These circumstances are sufficient to distinguish carbonic acid from all other gaseous acids which sulphuric acid expels from their compounds, with effervescence.—Many insoluble carbonates, on being treated with muriatic or nitric acid, under certain circumstances, produce no effervescence. This is particularly the case with the native compounds of carbonic acid with magnesia and lime (Bitterspar, Dolomite), and with protoxide of iron

(Spatheisenstein), which produce scarcely the slightest effervescence when treated in lumps with concentrated muriatic acid; yet they suffer decomposition when the mixture is heated, and produce an effervescence when exposed in a pulverised state to the acid. Carbonate of barytes, particularly that which is found native, is a substance which is scarcely affected in the slightest degree by common nitric acid; but as soon as the acid is diluted with water, the carbonate is dissolved with effervescence.

Ignition is incapable of decomposing the neutral carbonates which have a fixed alcali for base. The acid carbonates of fixed alcalies are converted by ignition into neutral carbonates, giving up one portion of their acid, but retaining with firmness the other portion. The carbonates of barytes and strontian suffer ignition without undergoing decomposition. The carbonate of lime, on being very strongly ignited in a small platinum crucible over the spirit lamp with circular wick, loses only a small portion of its carbonic acid; but on exposure to a stronger heat, or by being subjected, while under ignition, to the action of a current of vapour of water, it is deprived of the whole of its carbonic acid. All other carbonates are deprived by heat of their carbonic acid; some of them by a very moderate heat. Acids, or oxides which play the part of acids, but which are insoluble in water, such as silicic acid, titanic acid, tantalic acid, peroxide of tin, &c., cannot, in consequence of their insolubility, effect the expulsion of carbonic acid from the carbonates, while in solution; but these substances are capable of expelling the carbonic acid, when submitted to fusion with the alcaline carbonates.

When the carbonates of alcalies are mixed and strongly ignited with charcoal powder, they suffer decomposition; the carbonic acid is converted by the charcoal into carbonic oxide, which flies off in the state of gas.

The neutral carbonates which are soluble in water, give a strong blue colour to reddened litmus paper. Even the solutions of acid carbonates give a blue colour to reddened litmus paper, but the action is weaker.

The carbonates are readily distinguished from other salts by effervescing and disengaging an inodorous gas, on being treated, either in a dry state or in solution, by acids which are soluble in water.

IX. SILICIC ACID.

Pure silicic acid, prepared factitiously, is a white powder, which grits between the teeth. It occurs in a crystallised state in nature, constituting the mineral called Rock crystal; it also occurs in a massive state, forming Quartz. It is then generally of a white colour, but this is often affected by the presence of very slight traces of iron or manganese. Both rock crystal and quartz scratch glass feebly; but they are softer than the Diamond and some of the other gems.

Silicic acid, in the state in which it occurs in nature, is insoluble in water and in nearly all acids. The factitiously prepared silicic acid is also, after ignition, insoluble in water and in most acids. In consequence of this insolubility, it is unable to expel the carbonic acid from carbonates in solution, so that it produces no effervescence in such solutions. But when silicic acid is exposed with alcaline carbonates to a red heat, the mixture fuses, and the silicic acid combines with the base and expels the carbonic acid with effervescence. If, therefore, silicic acid is dropped into carbonate of potash or carbonate of soda while ignited and in a melted state, the solution effervesces in the same manner as when the solution of an acid is poured into the solution of a carbonate.

Of all the acids, *Hydrofluoric Acid* is the only one by which the ignited or the native pulverised silicic acid can be dissolved with facility. The more concentrated the aqueous solution of the hydrofluoric acid is, the more easily is the dissolution of the silicic acid effected. When the hydrofluoric acid is so strong as to fume in the air, it produces so much heat on dissolving the silicic acid, that the mixture boils spontaneously. None but metallic vessels dare be employed in this experiment. Glass must never be used, since the silicic acid which enters into the composition of glass, is equally attacked by hydrofluoric acid.

Silicic acid, previous to ignition, or at least, before it has been very strongly dried, is often slightly soluble both in water and in acids. When silicic acid is separated from chloride of silicium, or, better, from fluoride of silicium, by decomposition in water, a portion of the silicic acid dissolves in the water. The resulting solution is however quite tasteless, and totally without action on the colour of litmus paper. The presence of silicic acid is detected in this solution, by evaporating the liquid to dryness and treating the dry mass with water. The silicic acid then remains behind, in a state of insolubility.

The dried but not ignited silicic acid is readily dissolved on being heated in a solution of *Potash,* and the resulting solution does not gelatinise upon becoming cool. The dried silicic acid likewise dissolves with ease when heated in solutions of *Carbonate of Potash* or *Carbonate of Soda;* but the solutions so produced, stiffen upon becoming cold, to an opalescent jelly, which is so much the thicker, and is produced so much the quicker, in proportion as the solution is the more concentrated. Solutions of pure and of carbonated fixed alcalies are also capable of dissolving the ignited silicic acid; but the ignited acid is dissolved with much more difficulty than that which has not been ignited.

The silicates which contain an alcali, and have a great excess of base, are soluble in water. The more sllicic acid these compounds contain, the more difficult are they of solution in water; and when they contain a great excess of acid, they are quite insoluble, not only in water, but in acids, excepting always the hydrofluoric acid. An example of an insoluble silicate containing a great excess of acid, is afforded by glass. If the fixed alcaline silicates which contain a great excess of base are dissolved in a large quantity of water, and the solution is supersaturated with muriatic acid or any other acid, we do not obtain a precipitate of silicic acid, because the alcaline silicate dissolves in the diluted acid. But when the acid solution is evaporated to a certain degree of concentration, and is then permitted to cool, the silicic acid separates in the form of a transparent jelly, very similar in appearance to the jelly produced by cooling a solution of animal glue in boiling water. If a siliceous jelly of this description is mixed with water, the greater part of the silicic acid is deposited in the form of insoluble delicate flocks; but a portion of the acid redissolves in the water, the reason of which is that such an evaporation as that spoken of above, is not sufficient to effect the complete decomposition of the silicated alcali held in solution by the acid. If, however, the siliceous jelly is evaporated to perfect dryness, the dry residue, upon being treated with water, leaves the whole of the silicic acid undissolved.

When the basic alcaline silicate contains a somewhat greater quantity of silicic acid, but is still soluble in water, the supersaturation of the aqueous solution by muriatic acid, precipitates a portion of the silicic acid, in the state of delicate insoluble flocks, while another portion of the silicic acid remains dissolved in the acid solution. This solution, upon being evaporated, produces a jelly, and does not give up the whole of the silicic acid, unless it be evaporated to perfect dryness, upon which the silicic acid remains behind when the dry residue is treated with water. The more dilute the aqueous solution of a basic alcaline silicate of the description alluded to, the less silicic acid is separated by supersaturating the solution with muriatic acid. When such a solution is very concentrated, and contains a pretty large proportion of silicic acid, the latter is separated in such quantity on the addition of muriatic acid, that the whole solution runs into a thick lump.

The basic compounds formed by silicic acid with barytes, strontian, and lime, behave in the same manner as the basic silicates of alcalies, at least towards acids. When they are treated with muriatic acid, they give up the greater part of their silicic acid, but retain a portion in solution; when, too, the acid solution is concentrated by evaporation, the silicic acid forms a jelly; but the whole quantity of the silicic acid can be obtained only by evaporating the solution to dryness, and treating the dry residue with water.

The compounds formed by silicic acid with all other bases are insoluble in water. With respect to their behaviour towards acids, they may be divided into two classes: Some of them can be decomposed by stronger acids, for example, by concentrated muriatic acid; while others withstand the action of the strongest acids.

Those silicates which are decomposable by muriatic acid, exhibit different phenomena during their decomposition: When the finely pulverised compound is treated in the cold with concentrated muriatic acid, it is often decomposed on a sudden; a great deal of heat is disengaged, and the whole mixture runs into a gelatinous lump. If water is then added, the bases which were previously combined with the silicic acid, dissolve in the water in the state of metallic chlorides, while the free silicic acid remains behind, in the form of delicate flocks. There are a number of native silicates which are particularly remarkable for the manner in which they suffer this sort of decomposition. They are called Zeolites. Of these, it is the zeolites which contain water of crystallisation, which exhibit the above phenomena in the most striking manner. It is remarkable, that after these substances have been ignited, they are in most cases no longer susceptible of decomposition by muriatic acid.—Often, on the contrary, the finely pulverised silicates can be decomposed only by a prolonged digestion with muriatic acid, on which occasions they produce neither a gelatinous lump nor a jelly.

The silicates which withstand the action of acids, are decomposed by alcalies. The silicate, in a finely pulverised state, is ignited with three or four times its weight of carbonate of potash or carbonate of soda. During the ignition, carbonic acid gas is expelled from the carbonate, and the silicate is decomposed by the alcali. The silicate and pulverised carbonate of alcali are mixed and ignited in a platinum crucible. If the compound contain a large proportion of silicic acid, the mass afforded by the ignition is fused; but if it contain only a small proportion of acid, the mass is a mere conglomerate. The ignited mass is afterwards treated with diluted muriatic acid, upon which the bases which had been in combination with the silicic acid, dissolve in the state of chlorides, while the greater part of the silicic acid rests undissolved. The portion of silicic acid which dissolves in the muriatic acid, can be obtained by evaporating the acid solution. It forms a jelly when the solution is at a certain point of concentration. When the compound submitted to examination contains but a very small quantity of silicic acid, it often happens that the ignited mass dissolves in the diluted muriatic acid, without residue.

Many silicates appear at first to be indecomposable by acids; but when they are exposed to a prolonged digestion, and particularly when the operation is performed with sulphuric acid, diluted with a small quantity of water, the decomposition is fully effected. Sulphuric acid can be made to decompose nearly all the silicates by a prolonged digestion.

A few silicates are susceptible of decomposition, neither by solution in acids, nor fusion with carbonated alcalies. The decomposition of these compounds is effected by mixing them, in a very finely levigated state, with three times their weight of pure potash, and exposing the mixture, in a silver crucible, to ignition.

Of the siliceous compounds which occur in nature, the following can be completely decomposed by muriatic acid.

	German Names.	*English Names.*
1	Apophyllit	Apophyllite
2	Natrolith	Natrolite
3	Scolezit	Scolezite
4	Mesolith	Mesolite
5	Mesole	Mesole
6	Analcim	Analcime
7	Laumonit	Laumonite
8	Kaliharmoton	Potash-Harmotome
9	Leucit	Leucite
10	Elaeolith	Elæolite
11	Sodalith	Sodalite
12	Cronstedtit	Cronstedtite
13	Ilvait	Lievrite
14	Gehlenit	Gehlenite
15	Scapolith	Scapolite
16	Tafelspath	Tabular Spar
17	Nephelin	Nepheline
18	Chabasit	Chabasite

	German Names.	*English Names.*
19	Pectolith	Pectolite
20	Okenit	Okenite
21	Davyn	Davyne
22	Gadolinit	Gadolinite
23	Allophan	Allophane
24	Helvin	Helvine
25	Datholith	Datholite
26	Botryolith	Botryolite
27	Haüyn	Haüyne
28	Nosian	Nosiane
29	Lasurstein	Lazulite
30	Eudialith	Eudialite
31	Orthit	Orthite
32	Kieselzinkerz	Electric Calamine
33	Dioptas	Dioptase
34	Meerschaum	Meerschaum
35	Kieselmalachit	Copper Green
36	Stilbit	Stilbite
37	Epistilbit	Epistilbite
38	Heulandit	Heulandite
39	Anorthit	Anorthite
40	Titanit (Sphen)	Sphene
41	Pyrosmalith	Pyrosmalite
42	Cerit	Cerite
43	Cerin	Allanite
44	Uranpecherz.	Pitchblende.

The first named 34 of these compounds, when pulverised and treated with muriatic acid, produce a jelly. This is not the case with the last ten. Some of the latter can only be completely decomposed by muriatic acid, by being very finely pulverised and undergoing a long continued digestion at a strong heat. Most of them, though not all, withstand the action of acids after they have been ignited. Some, however, and particularly some of the last named, can be decomposed by acids even after ignition.

The following native compounds of silicic acid, either withstand the action of acids altogether, or are decomposed with so much difficulty, even when they have been pulverised, that their analysis must not be attempted by means of acids. It is necessary to decompose them by fusion with carbonate of potash.

	German Names.	*English Names.*
1	Feldspath	Felspar
2	Albit	Albite
3	Rhyacolith	Rhyacolite
4	Petalit	Petalite
5	Spodumen	Spodumene
6	Natronspodumen	Soda-Spodumene
7	Labrador	Labrador Felspar
8	Andalusit	Andalusite
9	Barytharmoton	Barytic-Harmotome
10	Olivin	Olivine
11	Prehnit	Prehnite
12	Rothbraunsteinerz	Red Manganese-ore
13	Glimmer	Mica
14	Lepidolith	Lepidolite
15	Talk	Talc
16	Chlorit	Chlorite
17	Pinit	Pinite
18	Achmit	Achmite
19	Amphibol	Amphibole
20	Anthophyllit	Anthophyllite
21	Pyroxen	Pyroxene
22	Diallage	Diallage
23	Schillerstein	Schillerspar
24	Epidot	Epidote
25	Idocras	Idocrase
26	Granat	Garnet
27	Dichroit	Dichroite
28	Staurolith	Staurolite
29	Smaragd	Emerald
30	Euclas	Euclase
31	Turmalin	Tourmaline
32	Axinit	Axinite
33	Topas	Topas
34	Chondrodit	Chondrodite
35	Picrosmine	Picrosmine
36	Karpholith	Carpholite
37	Speckstein	Steatite

	German Names.	*English Names.*
38	Serpentin	Serpentine
39	Bimstein	Pumice
40	Obsidian	Obsidian
41	Pechstein	Pitchstone.

To these belong also the various kinds of factitious glass, and the compounds which are termed false gems.

Of the siliceous compounds which withstand both the action of acids and the fusion with carbonate of potash, and which are decomposable only by ignition with pure potash, only three occur in nature. These are:

	German Names.	*English Names.*
1	Zircon	Zircon
2	Cyanit	Cyanite
3	Cymophan	Cymophane.

Before the *Blowpipe,* silicic acid behaves as follows: It does not dissolve in a bead of microcosmic salt, even when the heat is very long sustained, or it dissolves therein, if at all, in extremely small proportion. During the ignition, the silicic acid swims in the fluid glass, and forms a transparent inflated mass, which can be better observed during the fusion than after the cooling. When a silicate is treated with microcosmic salt, before the blowpipe, the base dissolves in the flux, and the silicic acid swims undissolved in the resulting glass.—In borax, on the contrary, silicic acid dissolves completely, yet very slowly.—With soda, on charcoal, before the blowpipe, silicic acid fuses to a perfectly clear bead, while carbonic acid gas is disengaged with effervescence. There are but few substances which produce a bead, by fusion with soda before the blowpipe; and of these substances, silicic acid alone produces with soda a transparent, clear, and colourless glass: this property, therefore, is strongly characteristic of silicic acid. Even when the silicic acid contains a small quantity of an earth, it still fuses to a clear glass with soda. This, for example, is the case with felspar. But the more earth a silicate contains, or, to speak more generally, the greater the proportion of any non-alcaline base which it contains, so much the more infusible is the compound [illegible] soda, and this is particular [illegible] the soda is [illegible] (Berzelius: Ueber die Anwendung des Löthrohrs, p.

Silicic acid is distinguished from other substances by being insoluble in acids after ignition, in all acids e[illegible] hydrofluoric acid. Its compounds are distinguished [illegible] other substances, more especially by their beh[illegible] before the blowpipe with microcosmic salt and soda [illegible] by any other character.

X. CHROMIC ACID.

The presence of chromic acid in the chromates, these are obtained in the solid state, is recognised l following characters:

Dissolved in borax or microcosmic salt, on cha before the *Blowpipe*, they produce a glass which acc both in the outer and inner flame, a beautiful em green colour. The colour is best exhibited when the is cold. It is to the presence of oxide of chromiu this green colour is attributable. When the com under examination contains, in addition to chromic a metallic oxide capable alone of strongly colourin blowpipe fluxes, the green colour which characterises mium may experience considerable modification. (ZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 80.)

If a chromate and a chloride be ground together, m with concentrated sulphuric acid in a glass tube clo one end, and warmed, they effervesce and disengage gas, which fills the upper part of the tube.—If a br be employed, instead of a chloride, a gas is disen which possesses nearly the same colour.

Mingled with *Muriatic Acid* and heated, the chro disengage chlorine, which can be distinctly known odour and also by its colour. The experiment is m a white glass tube closed at one end. The muriati quires a dark green colour during the process, on ac he oxide of chromium which is formed and dissol

When chromates are heated with a mixture of mu acid and alcohol, the reduction of chromic acid to oxide of chromium is effected still more rapidly; the solution assumes a dark green colour, and disengages chlorine ether.

The chromates in solution are detected by the characteristic coloured precipitates which they produce with solutions of certain metallic oxides. These precipitates have been described under the respective metallic oxides, in the preceding pages.

If solutions of chromates are acidulated with an acid, and then tested with *Liquid Sulphuretted Hydrogen*, the solutions change colour, and finally become green. After some time, sulphur begins to separate, and the solutions appear milky. If the whole be warmed a little, this effect is hastened. It will be understood, that in this experiment no metallic oxide must be present which can be precipitated or changed by liquid sulphuretted hydrogen.—The liquid, filtered from the sulphur, contains oxide of chromium in solution. Upon the addition of ammonia, the latter is precipitated with a light green colour. A solution of caustic potash likewise produces a light green precipitate, which an excess of the caustic potash redissolves. By simply boiling the potash solution, the oxide of chromium is again precipitated.

XI. ACIDS OF ARSENIC.

a. ARSENIC ACID.

Arsenic acid, in the soluble arseniates, when these are presented in the solid state, can be detected by the following experiments:—

Mingled with soda, and heated on charcoal, in the inner flame of the *Blowpipe*, they develope the well known odour of garlic which characterises the vapour of metallic arsenic. Mingled with charcoal powder and a little boracic acid, and heated in a glass tube closed at one end, they deposit on the cold part of the tube a metallic mirror of arsenic, the presence of the slightest trace of which can be distinctly recognised by the characteristic odour produced by heat.

In solutions, the arsenic acid of the arseniates can be detected as follows:—

Liquid Sulphuretted Hydrogen, or a current of *Sulphuretted Hydrogen Gas* produces in acidulated solutions of the arseniates, a bright yellow precipitate. The solutions are best acidulated by muriatic acid. The precipitate is not produced immediately, but only after very long reposure: the reaction is hastened by mixing with the solution, an excess of liquid sulphuretted hydrogen and boiling the mixture. This precipitate is easily soluble in hydrosulphuret of ammonia. It is discriminated by this character, from the precipitate produced by liquid sulphuretted hydrogen, in solutions of oxide of cadmium.

Hydrosulphuret of Ammonia produces no precipitate in solutions of neutral arseniates. But if an acid is added to the mixture, and the best acid to employ is muriatic acid, then a bright yellow precipitate is produced, under disengagement of sulphuretted hydrogen gas. This precipitate, however, does not appear immediately, but its production is hastened by the application of heat.

A solution of *Nitrate of Silver* produces in solutions of arseniates, a brown precipitate. Were the solutions of the arseniates and of the nitrate of silver both neutral, the liquid which remains above the brown precipitate reddens litmus paper. The brown precipitate is easily soluble in free nitric acid and in free ammonia.

Solutions of *Chloride of Barium* and *Chloride of Calcium, Lime Water,* and solutions of *Acetate* and *Nitrate of Lead,* behave towards solutions of arseniates in the same manner as towards solutions of phosphates, excepting that the precipitates of arseniate of barytes and arseniate of lime are much more easily soluble in a solution of sal ammoniac than the corresponding phosphates of those earths, while, on the contrary, they are more difficultly soluble when the solution contains free ammonia. It must farther be observed, that the arseniate of lead produced by precipitating the solutions of arseniates by acetate or nitrate of lead, behaves before the blowpipe in a manner quite different from the phosphate of lead. Heated on charcoal, in the flame of the blowpipe, the arseniate of lead gives out a thick smoke and an arsenical odour, and is reduced to metallic lead.

Of the preceding experiments, those with the blowpipe and liquid sulphuretted hydrogen taken together, give the most decisive result. As to the latter, it must still be remarked, that it is possible to confound the precipitate produced by sulphuretted hydrogen gas in acid solutions of arseniates, with that produced by the same reagent in acid solutions of peroxide of tin, since both are redissolved, on the addition of hydrosulphuret of ammonia.

b. ARSENIOUS ACID.

The salts of arsenious acid, considered with respect to their behaviour with certain reagents, have much resemblance with those of arsenic acid.

When present in the solid state, if mingled with soda, and heated on charcoal, in the inner flame of the *Blowpipe*, they behave precisely like the arseniates, and produce the well-known odour of garlic which characterises the vapour of metallic arsenic.

Mingled and heated with charcoal powder and boracic acid, they exhibit the same phenomena as the arseniates.

In solutions which have been acidulated by an acid, and best by muriatic acid, they produce with *Liquid Sulphuretted Hydrogen*, or with a current of *Sulphuretted Hydrogen Gas*, the same appearances as are produced in solutions of the arseniates. Nevertheless, in the present case, the precipitate is of a deeper yellow colour, and is produced much more readily than in solutions of the arseniates; it is even easily formed without warming the liquid. The precipitate is easily soluble in hydrosulphuret of ammonia, and in alcalies.

Hydrosulphuret of Ammonia produces no precipitate in solutions of the neutral arsenites; but if a little muriatic acid be added to the mixture, a discharge of sulphuretted hydrogen gas takes place, and a yellow precipitate is produced.

A solution of *Nitrate of Silver* produces in solutions of arsenites, a yellow precipitate. By means of this reagent, therefore, the arsenites can be well distinguished from the arseniates, with which the nitrate of silver produces a brown precipitate. On account of the colour, this yellow precipitate might be confounded with the yellow precipitate which solutions of oxide of silver produce in solutions of phosphates; more especially as both of these precipitates are soluble in free ammonia. Yet the precipitate produced in solutions of arsenites is distinguished from that formed in solutions of phosphates by being more easily soluble in weak acids.

Solutions of *Chloride of Barium,* of *Chloride of Calcium,* and of *Free Lime,* produce in solutions of the arsenites, white precipitates, which are pretty easily soluble in a solution of muriate of ammonia.—Solutions of *Acetate* and *Nitrate of Lead* also produce white precipitates.

C. NON-METALLIC BODIES.

I. CHLORINE IN CHLORIDES.

If the chlorides are presented in the solid state, they can be recognised by the following characters:

When mixed with concentrated *Sulphuric Acid* and warmed, they effervesce and disengage muriatic acid gas; and when a glass rod, moistened with liquid ammonia, is held over the mixture, white vapours are formed. Among the soluble chlorides, there are two, however, with which this is not the case: Perchloride of mercury is not decomposed by sulphuric acid; and protochloride of tin disoxidises the sulphuric acid.

Mingled with *Peroxide of Manganese,* or with *Red* or *Brown Oxide of Lead,* and with concentrated sulphuric acid, they disengage chlorine gas, which is detected by its characteristic odour, or when it is produced in greater quantity, by its action on moistened litmus paper, which it bleaches.

Before the *Blowpipe,* the chlorides, according to Berzelius, are detected by adding a small portion to a glass previously formed by fusing deutoxide of copper with microcosmic salt, and exposing the whole to the blowpipe flame; which then becomes of a blue colour. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 108.)

In their solutions, the chlorides are recognised by the white precipitate they produce with a solution of *Nitrate of Silver*. This precipitate appears flocculent when in great quantity, acquires a dark violet colour at the surface when exposed to the action of light, is insoluble in diluted nitric acid, but very easily dissolved on the addition of caustic ammonia. By the formation of this precipitate, the presence of chlorides in solution is very easily detected.

II. BROMINE IN BROMIDES.

Bromine in the bromides is distinguished by the following characters:

Before the *Blowpipe*, a bromide, when added to a bead formed of microcosmic salt and oxide of copper, and heated, gives a blue colour to the flame, just as is the case with chlorides under the same circumstances: yet the colour which is communicated to the flame by the bromides, tends more to greenish. (BERZELIUS: *Ueber die Anwendung des Löthrohrs*, p. 109.)

When the bromides are heated with concentrated *Sulphuric Acid* in a glass tube closed at one end, they disengage gaseous bromine, which fills the cold part of the tube. This gas is easily recognised by its yellow colour, which resembles that of nitrous acid gas. It can be seen very well by daylight, but not so well by candlelight. There are produced at the same time, in this experiment, sulphurous acid and hydrobromic acid. Some of the bromides cannot be decomposed in this manner by sulphuric acid, for example, the perbromide of mercury.

In solution, the bromides are discovered by heating them with nitric acid, which produces a disengagement of yellow vapours of bromine gas, which can be recognised by the odour and colour. The solution is rendered brown. The addition of nitric acid to the solution of a bromide, produces no change of colour unless the mixture is heated.

Free bromine communicates to *Starch* solution a brown colour. Solutions of bromides act in the same manner, yet only under the conditions which give to solutions of iodides the power of producing a blue colour. But this brown colour is so little characteristic, that it only serves to distinguish bromine from iodine.

Solutions of bromides, like solutions of chlorides, produce in silver solutions, a white precipitate, which is insoluble in diluted nitric acid, but soluble in ammonia. It is, however, more difficultly soluble in ammonia than chloride of silver is. Solutions of bromides produce in solutions of protoxide of mercury a white or yellowish precipitate, and in solutions of protoxide of lead, a white precipitate. The latter is distinguished from precipitated chloride of lead, by remaining undissolved when a large quantity of water is added.

The best way by which the analyst can convince himself of the presence of bromides in solutions, is by means of the white precipitates afforded with solutions of protoxide of mercury, protoxide of lead, and oxide of silver; yet as chlorides produce the same precipitates, the bromides can be easily mistaken for chlorides. The one can be distinguished from the other by boiling the precipitate with concentrated sulphuric acid, whereupon, bromide of silver disengages vapours of bromine, while chloride of silver, on the contrary, produces muriatic acid gas.—Solutions of bromides cannot be mistaken for solutions of iodides, if they be tested with starch and nitric acid. When iodides and bromides occur in the same solution, it is easy, by means of the starch solution, to detect the presence of iodine, but it is more difficult to prove that the compound contains bromine.

But when the compound which is to be examined for bromine, is insoluble in water, the presence of bromine is best detected when the bromide is treated with concentrated sulphuric acid, in the manner which has been described above.

III. IODINE IN IODIDES.

When in the solid state, iodine is detected in the iodides by the following experiments:

Before the *Blowpipe*, according to BERZELIUS, iodine can be detected in the iodides, in the same manner as chlorine in the chlorides. Oxide of copper is dissolved in microcosmic salt; a portion of the iodide is added to the bead, and the whole is heated before the blowpipe. The flame then assumes a beautiful emerald green colour. (BERZELIUS: *Anwendung des Löthrohrs*, p. 109.)

When iodides are heated with concentrated *Sulphuric Acid* in a glass tube closed at one end, they give out iodine, which fills the cold part of the tube, and is easily recognised by its characteristic violet colour. There is a simultaneous disengagement of sulphurous acid gas. In this manner, even those compounds of iodine and metals can be decomposed, whose corresponding chlorides are not decomposable by concentrated sulphuric acid; such, for example, as the periodide of mercury.

Many iodides, yet only those whose metals have but a slight degree of affinity for iodine, disengage violet vapours of iodine when they are heated to redness in contact with the air.

In solutions, iodides are recognised by the reddish brown colour which is produced on the admixture of liquid chlorine. When nitric acid of moderate strength is dropped into solutions of iodides, they become yellow: if the yellow solutions are then heated, they become reddish brown, disengage violet vapours of iodine, and after cooling deposit iodine in little black spangles. For the detection of a small quantity of iodine, it is best to employ a solution of *Starch* in hot water. Very slight traces of iodine can be very easily discovered, from the production, by means of this reagent, of a blue colour, which is so intense when large quantities of iodine are present, that it appears black. When a little starch and much iodine are in the solution, the colour produced is dark green. Hereby it is to be remarked, that it is free iodine alone which produces a blue colour with starch; and that when iodine is combined with hydrogen or with a metal, it possesses no such property. If, therefore, the operator wishes to detect iodine in the dissolved iodides by means of starch, he must add nitric acid or liquid chlorine to the solution, either before or after the admixture of the solution of starch. If liquid chlorine is used, it must not be added in excess, otherwise the blue colour is destroyed, as soon as it is produced. When much arsenious acid is present, no blue colour is produced by the mixture of iodine and starch; but it can be made to appear by the addition of a little diluted sulphuric acid. If a solution of perchloride of mercury be added to the solution of an iodide in so great an excess, that the periodide of mercury which is formed is completely redissolved by the excess of perchloride of mercury, the resulting solution exhibits no blue colour when nitric acid and solution of starch are added; nor, under those circumstances, is the blue colour producible by sulphuric acid. When a solution contains hydriodic acid or a metallic iodide, together with a great quantity of muriatic acid or of metallic chlorides, the addition of starch solution and nitric acid produces the blue colour in the cold; but if the mixture is boiled, the blue colour disappears.—The blue colour of iodine-starch is destroyed by solutions of alcalies, by sulphurous acid, phosphorous acid, sulphuretted hydrogen, &c.; but it can be reproduced by nitric acid.—If an excess of liquid chlorine has been added to the solution of an iodide, or if a solution contains iodine in the state of iodic acid, the addition of a solution of starch only produces the blue colour, when a little protochloride of tin is also added.

Solutions of the iodides produce in solutions of many metallic oxides, precipitates of various colours. These have been described in the preceding pages of this section, in which the behaviour of the metallic oxides towards reagents has been taken into consideration. Solutions of iodides are however not much to be recommended as a reagent for metallic oxides, because the precipitates which they produce are nearly all more or less soluble in an excess of the precipitant.

If a compound contains iodine combined with a metal, and if the compound is soluble in water, it is best to detect the iodine therein by starch solution and nitric acid. In the same manner can iodine be detected in every solution, even when it is accompanied by several other substances; nevertheless, it is necessary to have regard to those substances which can hinder the production of the blue colour. If, on the contrary, the compound which is to be examined for iodine, is insoluble in water, it is best to treat it with concentrated sulphuric acid, in order to disengage the violet gas of iodine. It is proper, in this case, to mingle the substance with a little peroxide of manganese, to hinder the production of sulphurous acid. If the quantity of iodine is too small to disengage distinct vapours of iodine, the operator can convince himself of its presence by the following process: The compound is mingled with peroxide of manganese, put in a flask, and treated with sulphuric acid. The operator then places, in the empty part of the flask, a paper that has been smeared with a thick solution or paste of starch; it is best to secure the paper by means of the stopper of the bottle. After some time, this paper becomes blue, even when the compound contains only very slight traces of iodine.

IV. FLUORINE IN FLUORIDES.

The fluorides, in the solid state, are recognised by the following characters:

A glass plate is covered with a coat of wax, by first warming the glass, and then melting and rubbing a little wax upon it. By means of a needle, letters are scratched through the wax, in such a manner as to make the glass visible. The glass plate so prepared is placed over a platinum crucible, containing a little of the fluoride recently mingled with concentrated sulphuric acid. The crucible is then so cautiously warmed, that the wax is not melted; after a short time, it is allowed to cool, and the wax is scratched from the glass plate. It is then found, that a strong corrosion of the glass has been effected where the letters were cut through the wax.

If a platinum crucible cannot be had, the pulverised fluoride is mingled with sulphuric acid to a pap, which is laid upon a glass plate prepared with wax, as before described. After the action has lasted some time, the mixture is washed off, the wax removed, and the corroded characters exposed to view. But for this method a greater quantity of the fluoride must be used.

Solutions of the fluorides, if not too much diluted, have, when sulphuric acid is added, the same corrosive action on glass.

The fluorides are very easily recognised in consequence of the powerful corrosive action which they exercise upon glass. They cannot be confounded with other substances.

V. SULPHUR IN SULPHURETS.

The sulphurets which are soluble in water, upon being treated with an acid, disengage sulphuretted hydrogen gas. If the solutions are not too much diluted, the disengagement of gas is accompanied by effervescence. This gas is so easily recognised from its well known offensive odour, that its disengagement upon the addition of an acid, renders the detection of sulphurets very easy. For the decomposition of the sulphurets, it is best to employ diluted muriatic acid or sulphuric acid, and not nitric acid.

The solutions of the sulphurets, which contain no excess of sulphur, behave towards solutions of the metallic oxides, like hydrosulphuret of ammonia, the habitudes of which have been described in the preceding pages.

PART II.

QUANTITATIVE ANALYSIS.

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This Second Part contains a description of the methods employed to separate from one another, and to determine the quantities of the constituents of compounds, more or less complex in their constitution, of which the qualitative examination has already been executed.

The description of the methods employed to effect the quantitative determination of the different substances, is so arranged, that the bodies which are called Bases come first, and are followed by those whose compounds possess Acid properties. Under Potassium, the quantitative determination of potash is described; under Sodium, which immediately follows, not only is the quantitative determination of soda described, but processes are introduced, which have for object the quantitative separation of soda and potash.

And this is the case with the whole series of simple bodies: first, the art of determining the quantity of the substance itself is described, and then follow the various methods according to which the compounds of the particular substance may be separated from all the compounds previously treated of. This disposition renders it possible to find, with ease, all the methods of separation which an operator may wish to consult, in arranging the plan of a quantitative analysis.

QUANTITATIVE ANALYSIS.

I. POTASSIUM.

Quantitative Estimation as Sulphate of Potash.—The quantity of potassium contained in a substance to be examined, when it does not require to be separated from any other base, is, in most cases, estimated as sulphate or carbonate of potash, or else as chloride of potassium. From the weight of these salts, the quantity of the potassium, or of the potash, is calculated according to the Tables of Berzelius. If potassium be contained in a solution as sulphate of potash, the solution must be evaporated by a gentle heat, to dryness, and the dry residue must be ignited and weighed. The evaporation can be best performed in a capsule of platinum; but when such a vessel is not to be had, or when the solution which is to be evaporated contains both nitric acid and muriatic acid, a capsule of porcelain must be employed. The dry mass is transferred, as accurately as possible and by the help of a platinum spatula, from the evaporating capsule, into a small counterpoised capsule or crucible of platinum. In order that nothing may be lost, the evaporating vessel must be washed out with water, and the washings added to the dry mass in the little platinum vessel, which must then be exposed to a careful evaporation until the whole of the salt becomes dry.—The sulphate of potash must, however, previous to its ignition, be exposed for a pretty long time to a strong heat, in order that, when it is subsequently heated to redness, it may not decrepitate, through which a considerable loss might be occasioned.

Conversion of Bisulphate of Potash into neutral Sulphate.—If the solution contained an excess of sulphuric acid, the substance obtained by the evaporation is bisulphate of potash, a substance which it is very difficult to deprive of excess of sulphuric acid, by mere ignition in a platinum crucible. But BERZELIUS has pointed out a method by which it can be converted into neutral sulphate both with ease and accuracy. The operator first exposes the salt to a gentle ignition; he then places in the platinum crucible a small piece of dry carbonate of ammonia, supporting it in such a position, on a piece of platinum foil, that the cover of the crucible can shut but loosely; he then applies a strong red heat. The excess of sulphuric acid contained in the bisulphate of potash easily flies off in an atmosphere of carbonate of ammonia, and neutral sulphate of potash alone remains behind. The mass, which at first was easily fusible, is now very difficultly fusible.

Estimation as Chloride of Potassium.—If potassium be contained in the solution as chloride of potassium, the solution is, in the same manner, evaporated to dryness, and the dry mass heated, in a little counterpoised platinum crucible, to incipient redness. It is absolutely necessary, during the heating, to place the cover upon the platinum crucible; because the too free admission of the air, while the mass is strongly ignited, is liable to cause the volatilization of a portion of chloride of potassium.

Treatment of Carbonate of Potash.—If the solution contain merely carbonate of potash, this can also be evaporated, and, as before described, ignited. But carbonate of potash so very easily attracts moisture from the air, that it is very difficult, after the salt is ignited, accurately to weigh it. It is therefore better, previous to the evaporation, to add muriatic acid to the solution; and then to calculate the quantity of carbonate of potash, from the weight of the chloride of potassium obtained. The operator could also first evaporate to dryness, ignite, and weigh the carbonate of potash; and then heat it in the platinum crucible with muriatic acid. After which, upon again very cautiously evaporating the whole to dryness, igniting and weighing the residue, he would be enabled, from the weight of the chloride of potassium, to correct the weight of the carbonate of potash. This method, however, demands a great deal of circumspection: the muriatic acid must be added to the carbonate of potash in the smallest possible quantities, in order that no spirting may be produced by the consequent extrication of carbonic acid gas, for a considerable loss might be thereby produced. While the acid is added, the crucible must be covered with a concave glass cover, that nothing may be lost during the effervescence. After saturation, the glass cover must be washed, the washings added to the solution, and the whole cautiously evaporated to dryness.

Estimation as Nitrate of Potash.—If the solution contain potash in combination with nitric acid, the solution must be, as before, evaporated to dryness. The dry residue, however, must afterwards be exposed to only a moderate degree of heat, to a temperature not much exceeding that of boiling water. It must be kept at that temperature till it be found that the weight is no farther reduced thereby. The nitrate of potash must never be heated till it fuses, because, by too long a fusion, it is capable of being partly decomposed. If the nitrate of potash contain small quantities of organic substances, the heated mixture detonates in consequence of the decomposition of a portion of the nitric acid. Part of the mass can in that case be easily projected from the crucible and lost.

Separation from Acids which are soluble in Alcohol.—If the potash be combined with any other acid, its quantitative determination must be effected after methods which will be circumstantially described hereafter. We shall in this place describe merely that process, according to which it can take place, when the acids with which it may be combined, are in a free state soluble in spirits of wine. The operator dissolves the compound which contains the potash in water, and adds to it a solution of chloride of platinum, in excess; he then very carefully evaporates the mixture till it is nearly dry. During the evaporation, a deposite is formed of the difficultly soluble double chloride of potassium and platinum. This occurs too, immediately on the addition of the solution of chloride of platinum, if the solution of the potash salt be not too dilute. The nearly-dry mass is mixed with spirits of wine, or the solution, when it has been reduced by evaporation to a very small volume, is mixed with alcohol. The chloride of potassium and platinum, which is insoluble in spirits of wine, is brought upon a weighed filter, is washed with spirits of wine, and carefully dried. From the weight of this double salt, the quantity of potash is subsequently calculated.—If the substance containing the potash be soluble in spirits of wine or in alcohol, the operator can add directly to the spiritous solution an alcoholic solution of chloride of platinum; thereupon the chloride of potassium and platinum precipitates: it is filtered from the solution and washed with spirits of wine.

II. SODIUM.

Quantitative Estimation as Sulphate, or Carbonate of Soda, or Chloride of Sodium.—When sodium is contained in a solution, in the state of a soda salt or of chloride of sodium, and is not combined with another substance from which it is necessary to separate it, the quantitative determination is effected in the same manner, as the quantitative determination of potassium. By the ignition of the neutral sulphate of soda, the operator has no decrepitation to fear. If it contain an excess of sulphuric acid, it must be treated with carbonate of ammonia, like the bisulphate of potash, in order to be converted into a neutral salt.—Chloride of sodium, like chloride of potassium, cannot be exposed to a strong heat, without suffering a loss by volatilization.—If soda is to be estimated as carbonate of soda, the operation can be performed much easier than the corresponding operation with carbonate of potash, since the carbonate of soda does not, so rapidly nor so easily as that substance, attract moisture from the air. It is proper to heat the carbonate of soda, in a counterpoised platinum crucible, until the salt fuses.

Separation from Potash.—When soda and potash occur together in a solution, they can be separated, according to BERZELIUS, by the following process: The operator converts both salts into chlorides, and evaporates the solution to dryness; he then transfers the dried chlorides into a counterpoised platinum crucible, heats the whole to incipient redness, and weighs the residue. The salt so obtained is mixed with 3¼ times its own weight of crystallised double chloride of sodium and platinum, which quantity is exactly sufficient, supposing the mass of salt under examination to consist merely of chloride of potassium, to convert the whole into the double chloride of potassium and platinum. The mixture is dissolved, in a platinum or porcelain capsule, in a very small quantity of water, and the solution is evaporated by a very gentle heat to dryness. The residue is next treated with spirits of wine, containing about 60 *per cent.* of alcohol. This dissolves the chloride of sodium and the excess of chloride of sodium and platinum, while the chloride of potassium and platinum resulting from the double decomposition, remains behind undissolved. The operator brings it upon a weighed filter, and washes it with spirits of wine. He then dries it by exposure to a very gentle heat, in which it must so long remain, that, after being repeatedly weighed, it no longer indicates a diminution of weight. From the weight of the resulting chloride of potassium and platinum, the quantity of chloride of potassium contained in the mass of chlorides from which it was separated, may be learned by calculation. The quantity of chloride of sodium is found, by deducting the weight of the chloride of potassium from the weight of the mixed chlorides. It is impossible, in this analysis, to employ the simple chloride of platinum with the same success as the chloride of sodium and platinum, because the chloride of platinum is very liable to be decomposed by alcohol.

Should the operator have a mixture of potash and soda in the state of sulphates, it is necessary to convert them into chlorides, before attempting to separate them by the process we have just described. In what manner this conversion of sulphates into chlorides can be best effected, will be described farther on, under the head of Sulphur.

III. LITHIUM.

Quantitative Estimation as Sulphate of Lithia.—When lithia has not to be separated from another base, it is determined quantitatively in the same manner as potash and soda.—If the lithia is combined with sulphuric acid, it is not necessary, as it is with the sulphates of potash and soda, to add carbonate of ammonia during the ignition of the salt; because there exists no bisulphate of lithia, and if an excess of sulphuric acid accompanies the neutral sulphate, it is easily driven off by heat.—As chloride of lithium easily deliquesces, and cannot on that account be accurately weighed, it is best to convert it into sulphate of lithia.

Separation from Soda and Potash by Phosphate of Soda. —When the quantity of lithia contained in a solution is very small, and when, also, it is accompanied by soda and potash, the quantitative determination is effected by BERZELIUS in a peculiar manner. (POGGENDORFF'S Annalen, Th. IV. p. 246.) He adds to the solution, pure phosphoric acid and pure phosphate of soda, the latter in excess, and then evaporates the mixture to dryness. When the evaporation has reduced the liquor to a certain degree of concentration, it becomes muddy, and after the complete drying up of the salt, there remains, upon dissolving the mass in cold water, a white powder. This powder does not dissolve, because the solution is rich in phosphate of soda; it sinks slowly to the bottom of the mother liquor. It is filtered, and washed with cold water; yet the washing must not be too long continued, because the powder, though in a very slight degree, is soluble in cold water. Hot water dare not be employed in washing, as it dissolves more of the powder than cold water does. This powder is the neutral double salt of phosphate of soda and phosphate of lithia. It must be dried, ignited, and weighed; and from the weight of the double salt, the quantity of the lithia must be calculated. (100 parts of the double salt contain 15,08 lithia).—It is absolutely necessary, that the solution from which lithia is to be thus separated, contain no other bases than alcalies. It is moreover necessary, after the salt has been ignited and weighed, carefully to examine it, in order to be fully convinced that the substance thus obtained is actually the double salt alluded to, since it could be easily confounded with the insoluble compounds formed by phosphoric acid with lime and magnesia. According to BERZELIUS, the best way to distinguish the phosphate of soda and lithia from those compounds, is to mix it with carbonate of soda and heat it on platinum foil till it fuses. It forms then a clear mass, which upon congealing becomes opaque. The earthy salts mentioned above, do not fuse with carbonate of soda. If the experiment be performed upon charcoal, the melted double salt and the carbonate of soda will be absorbed by the charcoal, but the earthy salts will remain upon the surface, while the carbonate of soda alone will be absorbed.

Separation from Potash by Chloride of Sodium and Platinum.—When lithia and potash are to be separated, the latter is precipitated exactly according to the method which was described, when treating of the separation of soda and potash, at p. 8. The solution which is filtered from the chloride of potassium and platinum, is mingled with a little muriatic acid and diluted with water; thereupon, the mixture is gently heated, till the greater part of the alcohol is expelled; and then, by a stream of sulphuretted hydrogen gas, the excess of platinum is precipitated. The solution is filtered, and the sulphuret of platinum is quickly washed with cold water. The filtered solution is warmed till it no longer smells of sulphuretted hydrogen, and the lithia is then precipitated, in the state of phosphate of soda and lithia, by the process which has been just described.—The solution which is filtered from the chloride of potassium and platinum can be analysed in another manner: namely, by evaporating the solution to dryness and igniting the dry residue, to decompose the chloride of platinum. The ignited mass must then be treated with water, the solution filtered from the reduced platinum, and the lithia precipitated from the filtered solution.

Separation from Soda.—When lithia is to be separated from soda, a simpler process can be employed. The operator first determines the weight of the two, either as sulphates or carbonates, or even as chlorides. He then dissolves the mixture, and precipitates the lithia as phosphate of soda and lithia. From the weight of this double salt, he calculates the quantity of the lithia salt; what is required to make up the original weight, is the quantity of the soda salt.

Separation from Soda and Potash.—When all the three alcalies, potash, soda, and lithia, are contained in one solution, and they are to be separated and their respective proportions ascertained, the operation commences with the determination of the weight of the mixed salts. The potash is first precipitated, as chloride of potassium and platinum; this double salt is weighed, and the corresponding quantity of potash is calculated. The excess of platinum remaining in the filtered solution, is separated either by a current of sulphuretted hydrogen gas, or by evaporating the liquid to dryness, and igniting the dry mass. In the next place, the lithia is precipitated as phosphate of soda and lithia, and the quantity of the lithia is calculated from the weight of this precipitate. The quantity of the soda contained in the mixture, is to be inferred from the loss of weight sustained by the whole.

IV. BARIUM.

Quantitative Estimation as Sulphate of Barytes.—Few substances can be quantitatively determined, or separated from many other compounds, with so much accuracy as barytes. The method of separation consists in gradually adding to a solution which contains barytes, diluted sulphuric acid, so long as precipitation is occasioned. The precipitate is sulphate of barytes, which is completely insoluble in water and in all diluted acids. The precipitate is washed, gently ignited, and weighed. From the weight obtained, the quantity of barytes is calculated. The filter can be burnt to ashes with the precipitate, and the operator has no reason to fear the reduction of the sulphate of barytes, by the charcoal afforded by the burnt paper. It is necessary to observe here, that, either before or after the addition of sulphuric acid, the solution from which barytes is to be precipitated should be warmed, and farther, that the filtration should never be commenced till the precipitate has completely subsided, and the supernatant solution become clear. If these precautionary measures are not employed, the sulphate of barytes commonly passes with the liquid through the filter, and forms a milky solution.

Estimation as Carbonate of Barytes.—Barytes can also be quantitatively determined as carbonate of barytes, yet this method is not susceptible of the extreme accuracy of the preceding, because the carbonate of barytes is not quite insoluble in water. But although the method of separation as sulphate of barytes stands far before this method, it is nevertheless impossible under particular circumstances to precipitate barytes otherwise than as carbonate of barytes. In these cases, it is thrown down from the liquid, by a solution of carbonate of ammonia. But as the common carbonate of ammonia is a mixture of carbonate and bicarbonate, and as the latter would produce a more soluble carbonate of barytes, the precaution is taken of adding to the barytic solution a little caustic ammonia, before the addition of the solution of carbonate of ammonia, and the whole is warmed upon the sand bath. The carbonate of barytes thus precipitated, is washed, but not with too much water; it is then dried, ignited, and weighed. It loses no carbonic acid during the ignition.

Separation from Alcalies.—When barytes is to be separated from alcalies, the whole compound is dissolved in water, or, if insoluble in water, in a diluted acid; for which purpose muriatic acid is best adapted. The barytes is then precipitated by an excess of sulphuric acid. The solution is filtered, and evaporated to dryness, and the quantity of the alcaline sulphates is determined in the manner which has been described above.

V. STRONTIUM.

Quantitative Estimation as Sulphate of Strontian.—Sulphuric acid does not precipitate strontian so completely as barytes, because the sulphate of strontian is not so completely insoluble in water as the sulphate of barytes. If, however, sulphuric acid be added to a compound in solution, containing strontian and an acid which is soluble in spirits of wine; and if alcohol be added to the mixture, and the resulting precipitate be washed with spirits of wine, then, the sulphate of strontian will be separated with very great accuracy, since it is incapable of being dissolved by spirits of wine.—In a great number of cases, however, the analyst is obliged to precipitate strontian by sulphuric acid from aqueous solutions, as for example, in the cases where other salts are present which are insoluble in spirits of wine.

Estimation as Carbonate of Strontian.—Although the quantity of strontian cannot, after the preceding method, be determined with so much accuracy as that of barytes can be determined, in similar circumstances, yet is this method still considerably better than that of precipitating strontian by carbonate of ammonia; since the carbonate of strontian, like the sulphate, is by no means insoluble in water. If, however, the operator should be desirous of following the latter method, he must add to the solution of strontian an excess of carbonate of ammonia previously mingled with a little free ammonia. He must then warm the whole upon the sand bath, filter the precipitated carbonate of strontian from the solution, and wash and ignite it. No loss of carbonic acid is occasioned by the ignition.

If the strontian of which the analyst wishes to determine the quantity, is dissolved in a liquid which contains no other base, the best method of proceeding is that which has been recommended for the determination of the alcalies.

Separation from Barytes.—Strontian is often separated from barytes by the following process: both substances are converted into chlorides, and the mixture is ignited and weighed; it is then treated with water-free alcohol, in which the chloride of strontium is soluble. Nevertheless, as the chloride of strontium is not very easily soluble in water-free alcohol; and as, on the other hand, the anhydrous chloride of barium is not entirely insoluble therein, this method is not much to be recommended. BERZELIUS has on this account recommended the following process (POGGENDORFF's Annalen, Th. I. p. 195): Both earths are dissolved in an excess of muriatic or acetic acid, and hydrofluosilicic acid is added to the solution. This produces a precipitate of barytes, while strontian remains in solution, in the free acid, in the state of fluoride of silicium and strontium. The precipitate of the fluoride of silicium and barium is not immediately deposited, but exhibits itself after some time, and has the form of little microscopic crystals. It must be washed and dried upon a filter previously weighed. The quantity of barytes is calculated from the weight of the fluoride of silicium and barium.—The filtered liquid, however, still retains in solution a very small quantity of the fluoride of silicium and barium. It is necessary to precipitate this portion of barytes by the addition of an exceedingly small quantity of sulphuric acid, of which the operator must be careful not to add so much as to act on the strontian in the solution. The small quantity of sulphate of barytes thus produced must be filtered from the solution, washed, gently ignited, and weighed. From the weight of the sulphate of barytes the quantity of barytes is calculated. The remaining solution is next to be mingled with an additional quantity of sulphuric acid, and evaporated to dryness; the dried mass, which is sulphate of strontian, is to be ignited and weighed. From the weight of the sulphate of strontian the quantity of strontian is calculated.

Separation from Alcalies.—Strontian can be separated from the alcalies, either by precipitating it by sulphuric acid, as sulphate of strontian, or by carbonate of ammonia, as carbonate of strontian. In both cases, the precipitate must be washed, dried, gently ignited, and weighed. The whole of the alcalies will be contained in the solution filtered from the precipitated strontian. If the strontian has been precipitated by sulphuric acid, the solution may be evaporated to dryness, and the dry mass ignited with a little carbonate of ammonia, by which means the alcalies are reduced to the state of neutral sulphates. If the strontian has been precipitated by carbonate of ammonia, the filtered solution may, in the same manner, be evaporated to dryness, and the dry mass be ignited. By this process the ammoniacal salts are volatilized; the fixed alcalies then remain behind, combined with the acid with which they were combined before they were separated from the strontian. This presumes, however, that the acid was not one of those which heat alone is capable of separating from bases and destroying. In this case, it is only necessary, after the expulsion of the ammoniacal salts, to add to the remainder a little sulphuric acid, by which means the alcalies are converted into sulphates.

VI. CALCIUM.

Quantitative Estimation as Sulphate of Lime.—Lime can be quantitatively estimated in the state of sulphate, if the process recommended in the case of strontian be followed. To the compound of lime with an acid which is soluble in spirits of wine, sulphuric acid and alcohol must be added. The sulphate of lime, which thereupon precipitates, must be filtered and washed with spirits of wine, in which liquid it is insoluble. It must afterwards be ignited. From the weight of the resulting sulphate of lime, the quantity of lime is learned by calculation.

Precipitation of Lime by Oxalates.—Suppose, however, that the solution containing the lime which is to be estimated, contains also other substances, especially such as are insoluble, or but difficultly soluble, in spirits of wine; suppose, too, that the lime be combined with an acid, with which it produces a compound soluble in water, it is then necessary to effect the precipitation as follows: In the first place, if the solution be not neutral, but acid, it must be somewhat supersaturated with ammonia, which, however, must not be added in such excess as to occasion precipitation. The operator must then add, by degrees, to the solution, a solution of oxalate of ammonia or of free oxalic acid, until it ceases to produce a precipitate. If free oxalic acid be employed as the precipitant, particular care must be taken that so much ammonia be present as is sufficient to prevent the solution from being rendered acid by the addition of the oxalic acid. When a neutral solution of lime is to be precipitated, it is merely necessary to employ the neutral oxalate of ammonia. The precipitate, which is oxalate of lime, deposits itself but slowly, and runs through the filter, and produces a milky solution. To prevent this mishap, the solution must be warmed before it is filtered, and the precipitate allowed sufficient time to fall to the bottom. The filtering dare not be hastened, for the oxalate of lime requires a considerable time to subside completely. In general, it is proper to allow the solution to remain undisturbed in a warm place for twelve hours, or even longer, before an attempt is made to filter it. The oxalate of lime, though completely insoluble in water, is soluble in acids; and, indeed, can be dissolved by oxalic acid. It is, consequently, of importance to ascertain whether, after the precipitation of oxalate of lime, the solution remain alcaline, or at least neutral. After the filtering, the oxalate of lime must be well washed, dried, and then ignited in a platinum crucible. There is, hereby, a pale blue flame exhibited, which is owing to the combustion of the carbonic oxide gas, produced by the decomposition of the oxalic acid. The hot mass acquires a greyish colour; yet, when the heat is increased, becomes again nearly white. The oxalate of lime is now converted into carbonate of lime, which, if the heat employed has not been too great, will have lost none of its carbonic acid. But as it is very easy for the heat to become so strong as to cause the disengagement of a portion of carbonic acid, it is proper to pay respect to this circumstance. The carbonate of lime must be weighed after the ignition, then uniformly moistened in the crucible with a few drops of a concentrated solution of carbonate of ammonia; after which, it must be cautiously dried, exposed to a very dull red heat, and again weighed. If the two weighings give the same result, it is a proof that no carbonic acid was disengaged during the first ignition; but if the second weighing intimates an increase of weight, it is very probable that this increase has arisen from carbonic acid derived from the carbonate of ammonia. From the weight of the resulting carbonate of lime, the quantity of lime is calculated.

Estimation as Carbonate of Lime.—The following is another method of precipitating lime: The operator adds to the diluted solution of lime, a solution of carbonate of ammonia, by which carbonate of lime is precipitated. But it is necessary to take the precaution of adding to the solution of carbonate of ammonia, before it is employed to precipitate the lime, a little caustic ammonia. After the precipitation, the whole must be allowed to digest a pretty long time in a warm place, and must not be filtered until the precipitate has completely fallen to the bottom. The carbonate of lime so obtained must, after drying, be very feebly ignited, or only strongly heated, to free it from moisture; it is then to be weighed.—Both the preceding methods, however, are impracticable, when the lime is combined with phosphoric acid, or indeed with any other acid with which it produces a compound that is insoluble in water, and can be held in solution only by an acid.

Separation from Strontian.—To separate lime from strontian, the analyst may employ the following method, which has been recommended by STROMEYER (*Untersuchungen über die Mischung der Mineralkörper*, T. I. p. 75.): The two earths are precipitated in the state of carbonates, and washed from the solution. A little water is poured upon them, and nitric acid gradually added, till the whole is dissolved. In order, however, to obtain a solution in as complete a state of neutrality as possible, that being a point altogether necessary to the success of this operation, the analyst must, towards the end of the process, not only add the nitric acid with a great deal of precaution, but also, previous to every addition of fresh acid, warm the solution until he perceives no farther action of the acid. The reason why the liquid must be warmed is, that when the solution begins to approach the point of neutrality, and at the same time is not very dilute, it is impossible completely to dissolve the earths in the cold, so as to form a neutral solution. When the solution is prepared, it must be put into a flask which can be well closed, and must therein be evaporated to complete dryness, whereupon the flask must be immediately closed. When the saline mass is cold, the operator pours upon it about twice its bulk of absolute alcohol, closes the flask immediately, and shakes it very frequently. At the same time, however, he must carefully avoid the application of heat. The nitrate of lime dissolves completely in the alcohol; but the nitrate of strontian remains undissolved. When the latter has completely subsided, the solution is passed through a filter which has been weighed; the nitrate of strontian is then brought upon the filter, and washed with absolute alcohol. During filtration, t[illegible]el must be carefully closed with a glass plate, to hinder the attraction of moisture from the air. The filter, with the nitrate of strontian, is thereupon dried; and from the weight of that salt, the quantity of the strontian is calculated. For the sake of greater certainty, the nitrate of strontian can be dissolved in water; the solution be mingled with sulphuric acid; and the whole be evaporated to dryness. The dried mass can then be heated to redness in a counterpoised platinum crucible or platinum capsule, and weighed. From the weight of the resulting sulphate of strontian, the quantity of strontian may be calculated.—The alcoholic solution which was filtered from the nitrate of strontian, and which still contains the nitrate of lime, is now diluted with water, and heated moderately upon the sand bath, until the whole of the alcohol has been driven away; the lime is thereupon precipitated by oxalate of ammonia. The oxalate of lime thereby produced, is treated in the manner which has been described above. There is, however, a shorter and simpler method of estimating the lime. This consists in adding sulphuric acid to the alcoholic solution filtered from the nitrate of strontian. There is then produced a precipitate of sulphate of lime, which requires to be washed with spirits of wine.

Separation from Barytes by Alcohol.—To separate lime from barytes, the analyst has the choice of two methods. According to the first of these, he commences by converting both earths into chlorides. If they are in the state of carbonates, he adds to them an excess of muriatic acid, and evaporates the solution to dryness. He then exposes the dry mass, in a counterpoised platinum crucible, to a strong red heat, and afterwards weighs it. If the solution in which the chlorides were dissolved, contained, as is very often the case, muriate of ammonia also, the chlorides of barium and calcium are freed from the latter substance by the ignition. When the chlorides have been weighed, they are transferred to a flask which can be closed by a stopper. They are therein treated with absolute alcohol, in which the chloride of calcium dissolves, while the chloride of barium remains undissolved. When the alcoholic solution of chloride of calcium has been filtered from the chloride of barium, and the latter has been washed on the filter with absolute alcohol, the operator dilutes the filtered solution with water, and gently heats it to drive away the alcohol. The lime is then precipitated by oxalate of ammonia: and the precipitated oxalate of lime is treated in the manner which has been described above. The lime can also be separated by a simpler process, which consists in adding sulphuric acid to the alcoholic solution, and in washing the sulphate of lime with spirits of wine. The chloride of barium, which was not dissolved by the alcohol, is to be dissolved in water, and precipitated by sulphuric acid, as sulphate of barytes.

Separation from Barytes by Sulphuric Acid.—But the above method, even when it is put into practice with great care, gives no very accurate result; because the chloride of barium, even when it has been freed from its water of crystallisation, is not altogether insoluble in absolute alcohol. There is, however, another method of separating lime from barytes, which affords a more accurate result, and which is moreover to be preferred, inasmuch as it is thereby quite immaterial in what acid the two earths may be dissolved; as it is, also, whether or not they be accompanied by alcaline salts. This method consists in diluting the solution which contains the two earths with a large quantity of water, and then adding sulphuric acid as long as it produces a precipitate. The substance precipitated is sulphate of barytes. As for the sulphate of lime which is produced at the same time, as it is not quite insoluble, but merely difficultly soluble in water, it remains completely dissolved, provided the solution has been previously diluted with a sufficient quantity of water. If this has not been the case, the precipitated sulphate of barytes contains more or less sulphate of lime. When the solution has been warmed, and the precipitate has completely subsided, it must be filtered, and well washed with water. When the precipitate contains much sulphate of lime, the washing, on account of the difficult solubility of the latter, must be continued for a very long time. The object is not promoted by the employment of warm water, because sulphate of lime is not more easily soluble in warm water than in cold. After the sulphate of barytes has been thoroughly washed, its weight is determined. The filtered solution is then saturated with ammonia, and the lime is precipitated by oxalate of ammonia. The oxalate of lime is treated in the manner which has been already described. —When barytes is separated from lime according to this method, the solution from which the barytes is precipitated by sulphuric acid, may be acid, since the sulphate of barytes is insoluble in all diluted acids; but, on the other hand, the solution of the earths dare not contain free ammonia, because, in that case, the sulphate of lime would be partly decomposed by the carbonic acid of the atmosphere, and carbonate of lime would be gradually deposited on the sides of the vessel; in consequence of which, the weight of the sulphate of barytes, supposing it not to have been previously filtered from the solution of sulphate of lime, would be apparently increased. If, therefore, such a solution contain free ammonia, it must be preparatively supersaturated by an acid.

Separation from Strontian and Barytes.—To separate lime from strontian and barytes, the following process is often adopted: They are all precipitated together in the state of carbonates, by a solution of carbonate of ammonia, mingled with a little caustic ammonia; the precipitation being assisted by heat. The precipitate is dissolved in muriatic acid; the solution is evaporated to dryness, and the dry mass is ignited. It is then treated with absolute alcohol, which dissolves the chloride of strontium and the chloride of calcium, but leaves the chloride of barium undissolved. The alcoholic solution is then mixed with water, and the alcohol is driven away by a gentle heat; thereupon, nitric acid is added to the solution, and the whole is evaporated to dryness; by which means, the chlorides are converted into nitrates, which can be separated by the process that has been given above.—It is better, however, when the operator has to analyse a solution containing the three earths, to precipitate the barytes by means of hydrofluosilicic acid, and to mix the filtered solution with sulphuric acid. Upon evaporating the mixture to dryness, and igniting the dry mass, he obtains a mixture of sulphate of strontian and sulphate of lime. This is mingled, in a platinum crucible, with three times its weight of carbonate of soda or carbonate of potash, and the mixture is melted. After the fusion, water is poured over the melted mass, and an insoluble substance is obtained, which consists of carbonate of strontian and carbonate of lime. To separate these from each other, the process must be employed which has been described at page 18.

Separation from Lithia, Soda, and Potash.—The separation of lime from the three fixed alcalies is very easy. The lime is precipitated by oxalate of ammonia; and the solution filtered from the oxalate of lime is evaporated to dryness. The dry mass is transferred to a counterpoised platinum crucible, is ignited, and weighed. By this process, the alcali is obtained in combination with the acid with which it was combined in the original solution; it being supposed that the alcaline salt is one of those which are not decomposable by heat. If, for example, the lime and alcali were dissolved in muriatic acid, the alcaline substance furnished by the above process would be chloride of potassium or of sodium, &c. The ammoniacal salts dissolved in the solution, as, for example, excess of oxalate or muriate of ammonia, are destroyed or volatilized during the ignition. It is necessary, however, to employ much precaution when lime has been precipitated by oxalate of ammonia from a solution containing sulphuric acid or sulphate of ammonia. If the quantity of sulphate of ammonia be considerable, it is difficult to avoid a loss. Upon being heated, the sulphate of ammonia is melted, decomposed, and volatilized; but while undergoing this change, it sputters about very much. It is advisable to evaporate the solution filtered from the oxalate of lime in a pretty large platinum capsule, and to ignite the dry mass in the same vessel, until nearly all the ammoniacal salts are driven away. The alcaline sulphate must then be carefully transferred into a little counterpoised platinum capsule, or into a platinum crucible, and the last portions must be washed out of the large capsule with water, and poured into the little capsule; the whole must then be evaporated to dryness, heated to redness, and weighed. During the ignition, a small quantity of carbonate of ammonia must be employed, to assist the disengagement of the excess of sulphuric acid which may be present. The operation is effected agreeably to the instructions which have been given at page 6.

VII. MAGNESIUM.

Quantitative Estimation of Magnesia.—The quantitative separation of magnesia is accompanied by many difficulties. This substance cannot be estimated with so much accuracy as the substances of which we have spoken hitherto.

Estimation as Sulphate of Magnesia.—When magnesia is contained in a solution, from which no other substance is to be quantitatively separated, and which, besides magnesia, contains no other fixed constituent, the best method of proceeding is to evaporate the solution to dryness, and to ignite the dry mass in a counterpoised platinum crucible. By this means, all the ammoniacal salts which the solution may contain, are driven away. Sulphuric acid, previously diluted with a little water, is then poured over the heated mass; the whole is again evaporated to dryness, and the dry mass is gently ignited, to drive away the excess of sulphuric acid. The substance left behind is neutral sulphate of magnesia. It is now weighed. From the weight of this salt, the quantity of the magnesia is calculated. If the original solution contained sulphuric acid, it is, of course, unnecessary to saturate the dry mass with this acid subsequently to the first ignition. When, however, ammoniacal salts are contained in the solution, the sulphuric acid must never be added until the ammoniacal salts have been driven away by heat. There would otherwise be much sulphate of ammonia produced, which is a thing that should be avoided; for, in consequence of its melting and sputtering about, it is difficult to expel that salt without expelling a portion of the fixed substance in company with it.

Precipitation by Carbonate of Potash and Phosphate of Ammonia.—When a solution contains magnesia, in company with other fixed substances, as for example, with potash salts, and the magnesia alone is to be quantitatively estimated, it is possible to precipitate this earth, by a solution of carbonate of potash, in the state of carbonate of magnesia. But, as the neutral carbonate of magnesia, which must necessarily be precipitated by neutral carbonate of potash, is decomposed by water in such a manner as to give rise to bicarbonate of magnesia, which is soluble in water, the operator must take the precaution, in order to provide against this circumstance, of boiling the magnesian solution with an excess of carbonate of potash. In spite of the boiling, however, a small portion of magnesia could still remain in solution. It is best, therefore, after mixing the magnesian solution with the carbonate of potash, and boiling the mixture, and even after the precipitation of the greater part of the magnesia, to transfer the whole into a porcelain capsule, or still better, into a platinum capsule, and to evaporate it, by a stronger heat, to dryness. Hereby, in order to avoid a loss by spirting, the mass must be stirred about, especially towards the end of the operation. Boiling water is afterwards poured over the dry mass, which leaves carbonate of magnesia undissolved. This solution is then filtered, and the precipitate is washed with hot water. The washing must, if possible, be continued uninterruptedly; yet, it should not be carried on too long, since the carbonate of magnesia is not altogether insoluble in water. It dissolves, however, more difficultly in hot water than in cold; on which account, the water employed for the washing should be as hot as possible. When the washing has been so long continued, that some drops of the water which has passed through the filter, upon being evaporated to dryness on platinum foil, leave only a slight stain, the carbonate of magnesia may be dried, ignited, and weighed. It loses its carbonic acid during the ignition, which, on that account, must not be too soon ended.—The solution filtered from the carbonate of magnesia still retains a small quantity of carbonate of magnesia. In order to determine the quantity of this remainder, a solution of phosphate of soda is first added, and then caustic or carbonated ammonia; and the whole is allowed to remain quiet for some time, in a warm situation. There is produced a larger or smaller quantity of subphosphate of ammonia and magnesia, which subsides, after some time, as a crystalline precipitate. This substance, according to BERZELIUS (*Lehrbuch*, Th. II. p. 651), is perfectly insoluble in a solution which contains phosphate of ammonia; but, in pure water, it dissolves in a slight degree; the washing must, therefore, not be too long continued. The precipitate is subsequently dried and ignited. This operation decomposes it; the water and ammonia which it contained are driven away, while neutral phosphate of magnesia remains behind. It is usual to calculate that this ignited precipitate contains precisely 40 per cent. of magnesia, although the neutral anhydrous phosphate of magnesia contains only 36·67 per cent. of magnesia. Yet, as the crystalline salt is somewhat soluble in water, and consequently suffers a loss by the washing, the true estimate is very nearly approached, by supposing the ignited salt to contain 40 per cent. of magnesia. The quantitative determination of magnesia would be too uncertain were the whole to be precipitated as subphosphate of ammonia and magnesia; but when it is first precipitated by carbonate of potash, in the manner which has been described above, and the traces which remain in solution are afterwards precipitated as subphosphate of ammonia and magnesia, the ignited remainder of the latter salt being calculated to contain 40 per cent. of magnesia, we arrive as near to an accurate determination of the quantity of magnesia, as it is possible to do by any process at present known.

In the precipitation of magnesia by carbonate of potash, there are several precautionary measures to be observed, the neglect of which commonly produces very great errors. If the magnesian solution contains a considerable quantity of muriate of ammonia, or of any other ammoniacal salts, the whole quantity of magnesia cannot be precipitated until the ammoniacal salts are totally decomposed. But this takes place only when an excess of carbonate of potash has been boiled with the solution for a considerable time. When the solution is evaporated to perfect dryness, all the ammonia volatilizes in the state of carbonate of ammonia. But those who are unused to analytical labours often deceive themselves in the quantity of carbonate of potash which should be added. In order to see whether a sufficient quantity of carbonate of potash has been added to the magnesian solution, the mixture is heated until it ceases to give out the odour of ammonia. A fresh quantity of carbonate of potash is then added, and the application of heat is continued. If this reproduces the disengagement of the ammoniacal odour, it shows that a sufficient quantity of carbonate of potash had not previously been applied. When the dry mass produced by the evaporation of the solution is treated with water, the new solution ought to give a very strong blue colour to litmus paper. Should the litmus paper remain unaltered, the solution must be mingled with another portion of carbonate of potash, and the evaporation to dryness be repeated.

Instead of carbonate of potash, the operator can, in all cases, make use of caustic potash, by which, indeed, magnesia is precipitated even better than by carbonate of potash. But the substance then obtained is pure magnesia, which is more easily soluble in water than carbonate of magnesia; though, like the latter substance, it is less easily dissolved by hot water than by cold.

Carbonate of soda cannot, with equal good consequences, be employed instead of carbonate of potash. Carbonate of magnesia, according to MOSANDER (POGGENDORFF'S *Annalen*, Th. v. p. 505), forms, with carbonate of soda, a double salt. This salt is decomposed, neither by boiling the solution, nor by evaporating it to dryness; while, on the contrary, the analogous double salt containing carbonate of potash and carbonate of magnesia, suffers decomposition thereby. The wash-water also dissolves much more of the double salt containing soda than of the simple carbonate of magnesia; yet, for all that, were carbonate of soda employed to separate magnesia, a great excess would be obtained in the analysis.

As it is a very difficult thing to determine with accuracy the quantity of magnesia, even when that substance is contained alone in a solution, so the difficulties become much more considerable when magnesia has to be separated from other substances, the whole of which have to be quantitatively estimated.

Separation from Lime by Oxalates.—When a solution contains lime and magnesia, the separation can be effected by a variety of processes, of which the following are those most frequently employed: If the solution, which contains the lime and magnesia, contain also muriate of ammonia, or other ammoniacal salts, which is a case of frequent occurrence, the solution must be properly diluted with water, and then mixed with caustic ammonia, of which the smallest possible excess must be present. If no ammoniacal salts are present, muriate of ammonia must be added to the solution; yet, if the solution be acid, it is unnecessary to add muriate of ammonia, because the saturation of the excess of acid with ammonia produces a sufficient quantity of an ammoniacal salt. No precipitate is produced when the ammonia is added, provided the solution holds a sufficient quantity of ammoniacal salt. If, however, a small precipitate appears, in consequence of a deficiency of ammoniacal salt, then an acid, for example, muriatic acid, must be added to dissolve the precipitate; and the solution must then again be supersaturated with ammonia, which will not again produce a precipitate. The solution being thus prepared, the lime is to be precipitated by oxalic acid, or by oxalate of ammonia. This is performed, with the precautions which have already been pointed out at page 16. The magnesia is not precipitated, in consequence of the presence of the ammoniacal salts, notwithstanding that the oxalate of magnesia is, of itself, very nearly insoluble in water. When the solution has been filtered from the oxalate of lime, the magnesia is separated by carbonate of potash, in the manner which has already been described.

Separation from Lime by Sulphate of Lime.—Another method of separating lime and magnesia, described by R. Phillips and Cooper (*Quarterly Journal of Science*, vol. VII. p. 392), is this: When the solution to be examined, contains not only lime and magnesia, but other fixed constituents, as, for example, alcalies, then the two earths are precipitated by carbonate of potash; the solution, with the reagent, being evaporated to dryness. Hot water is poured over the dry mass; and the carbonated earths are washed with boiling water. They are then cautiously supersaturated with diluted sulphuric acid, and the whole is evaporated to dryness. The dry mass is gently ignited, in a counterpoised platinum crucible, to expel the excess of sulphuric acid. If, on the contrary, the solution contains no other fixed constituents than lime and magnesia, and these earths are combined with acids which can be expelled by sulphuric acid, the solution is evaporated to dryness; and if any ammoniacal salts are present, the dry mass is ignited, to expel them. The mass is then treated with sulphuric acid, is evaporated, and again ignited, to drive away the excess of sulphuric acid. The ignited mass is weighed, and afterwards digested with a saturated solution of sulphate of lime. This solution merely dissolves the sulphate of magnesia, and leaves the sulphate of lime undissolved. The insoluble remainder is washed with a saturated solution of sulphate of lime, until it is thought that it cannot any longer contain sulphate of magnesia; thereupon, it is heated to redness, and weighed. From the difference in weight, the operator finds the quantity of sulphate of magnesia; and from the weight of the two sulphates he calculates the quantities of the earths. This method, which can be employed with advantage in many cases, is somewhat more uncertain than the one preceding. One cannot tell when all the sulphate of magnesia is washed out; and then the filter of the sulphate of lime remains saturated with a solution of the same substance, by which its weight must necessarily be a little increased.

The other methods of separating lime from magnesia may be passed over, for the results they afford are less satisfactory than the results afforded by the two methods which have been described.

Separation from Barytes and Strontian.—The separation of magnesia from strontian and barytes is accompanied by no difficulties. If they are contained in a solution, the strontian and barytes are precipitated as sulphate of strontian and sulphate of barytes; the solution is filtered, and the magnesia is either estimated as sulphate of magnesia, or precipitated by carbonate of potash. The precautions to be observed in the latter case have been described above. As sulphate of strontian is not so completely insoluble in water as sulphate of barytes is, this process is better adapted to separate magnesia from barytes than from strontian.

Separation from the Fixed Alcalies.—The separation of magnesia from the fixed alcalies is very difficult. The magnesia and the fixed alcalies are converted into sulphates, which it is very easy to do. The sulphates are gently ignited, then weighed, and dissolved in water. The solution so produced, is mixed with so much of a solution of acetate of barytes, that all the sulphuric acid is precipitated as sulphate of barytes. The mixture is warmed; the sulphate of barytes separated by filtration; the filtered solution evaporated to dryness; the dry mass ignited in a platinum capsule. Hereupon, the acetates undergo a change, by which they are converted into carbonates; and, according as the heat may be stronger or weaker, the carbonate of magnesia loses a greater or lesser quantity of its carbonic acid. Hot water is poured over the mass after ignition; the alcaline carbonates then dissolve; the carbonates of barytes and magnesia remain undissolved. The solution of alcaline carbonates is filtered from the insoluble remainder, and the latter is edulcorated with hot water. But the washing dare not be too long continued, for neither the carbonate of barytes nor of magnesia is altogether insoluble in water. The alcaline solution is evaporated to dryness, and the dry mass is ignited and weighed. The salts are then converted into chlorides; or, as they are then better capable of being weighed, into sulphates.—The carbonates of barytes and magnesia which remained undissolved in water, are dissolved in muriatic acid; the barytes is precipitated by sulphuric acid; the solution is filtered from the sulphate of barytes, and evaporated to dryness; the dry mass so obtained is ignited and weighed; it consists entirely of sulphate of magnesia. If the weight of the alcaline sulphates is now added to that of the sulphates of magnesia, the total must agree with the weight of the mixed sulphates, as determined before the separation.—It will be perceived, that this is a very round-about process, and that it can give no absolutely accurate result, because the carbonates of barytes and magnesia are not positively insoluble in water. Potash can be best separated from magnesia by this process; with soda and lithia it does not succeed so well. Soda, when in the state of a carbonate, forms, with carbonate of magnesia, a double salt, which is, however, decomposed when heated to redness, so that, upon washing with water, carbonate of soda dissolves, and magnesia remains behind. But in consequence of this combination, there can afterwards be more magnesia dissolved by the water than would otherwise be the case. The separation of lithia cannot be effected by this process with perfect accuracy, because the carbonate of lithia is very difficultly soluble in water. It is, in consequence, better, when lithia alone is to be separated from magnesia, to precipitate the latter by means of a solution of carbonate of soda. To do this effectually, the whole is evaporated to dryness, and hot water is poured over the dry mass. The insoluble double salt of carbonate of soda and carbonate of magnesia is filtered from the solution, washed with hot water, and then heated to redness: it is thus decomposed. The ignited mass is treated with water; carbonate of soda dissolves, and magnesia remains behind. Its weight is then determined.—From the solution filtered from the double salt, the lithia is to be precipitated as phosphate of soda and lithia, agreeably to the instructions given at page 10.

VIII. ALUMINUM.

Quantitative Estimation of Alumina.—Alumina is fully precipitated from its solutions by carbonate of ammonia, caustic ammonia, and carbonate of potash. The precipitate is very bulky, and difficult to be washed clean: the washing succeeds best with warm water. The precipitate shrinks together exceedingly as it dries; it must be extremely well dried before it can be ignited and weighed. The ignition must be performed with precaution, because dry alumina often decrepitates upon being heated, whereby a loss can be occasioned.

Of the above named precipitants, carbonate of ammonia is the best. It must consequently be always employed, when it is not necessary to avoid the presence of carbonic acid. Even when a neutral solution of alumina is precipitated by carbonate of ammonia or by any other alcaline carbonate, an effervescence is produced by carbonic acid, because this acid does not combine with alumina. Caustic

nia also precipitates alumina extremely well, and
be employed in a great number of cases where the
nate of ammonia cannot be made use of. It is neces-
o avoid setting too great an excess of caustic am-
to a solution, because a small quantity of alumina
thereby be dissolved. It is found that when the
itate is separated by filtration, and the filtered solu-
rarmed till the excess of ammonia is volatilized,
of alumina are often deposited, which however are
iderable in quantity and frequently almost impon-
le. The employment of carbonate of potash, as a
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t precipitates alumina completely, but it is extra-
urily difficult, indeed pretty nearly impossible, to
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shing; so that, upon weighing the alumina, a greater
it is obtained than is proper. When the operator
een obliged to precipitate alumina by carbonate of
h, it is necessary, if he is working upon an accu-
quantitative analysis, to redissolve the precipitated,
d and washed alumina, in an acid, for example, in
tic acid, and to precipitate it again by carbonate of
nia.

aration from Magnesia.—There are several methods
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by ammonia produces a sufficient quantity of an am-
ical salt to retain the magnesia in solution, when the
s of ammonia is added. The alumina is filtered and
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ot be avoided, probably in consequence of the chemi-
ffinity between magnesia and alumina, through which

the latter is enabled to carry down a portion of the former in a state of combination. To separate this small quantity of magnesia, the alumina must, while yet in a moist state, be treated with a solution of caustic potash. The best method of operating is to put the wet filter with the alumina into a glass, and to add a sufficient quantity of muriatic acid to dissolve the alumina; taking care, however, to avoid too great an excess of muriatic acid. Hereupon the solution is filtered, and the filter washed fully clean. To the solution in muriatic acid, a solution of caustic potash is added in excess, and the whole is heated in a porcelain capsule, or better in a platinum capsule. The alumina dissolves in the potash ley, while the small quantity of magnesia remains undissolved. The solution of the alumina can be effected in the cold, but it is always better to employ heat, which occasions a more perfect separation. The small quantity of magnesia is now filtered and washed; it is then, with the wet filter, put into muriatic acid, by which the magnesia is dissolved. The filter is properly washed, and the solution of the small quantity of magnesia is poured into the solution of the principal quantity of magnesia which, in the early part of the operation, was filtered from the precipitate produced by caustic ammonia. By the mixture of the two solutions, the whole quantity of the magnesia is brought together. It is then precipitated according to the process which has been described under the quantitative determination of magnesia.—The quantity of the alumina dissolved in the potash ley, still remains to be determined. Such a quantity of muriatic acid is added to the solution, that the alumina, which at first precipitates, again dissolves; a slight excess of the acid is sufficient for this purpose. From the solution in muriatic acid, the alumina is precipitated by ammonia, or better by carbonate of ammonia. This method of precipitating alumina from its solution in caustic potash is far preferable to another which is cheaper and generally employed. It consists in adding to the alcaline solution of alumina, a solution of muriate of ammonia; the potash is thereupon converted into chloride of potassium, the alumina is precipitated, and the ammonia becomes free. But the great quantity of free ammonia which is produced, can act in such a manner as to retain a portion of alumina in solution, while, on the other hand, according to the observation of BERZELIUS, the precipitated alumina carries a little potash down with it, and thereby acquires an increase of weight.

Another method of separating alumina from magnesia might consist in dissolving both earths in an acid, for example, in muriatic acid, of which, however, an excess should be avoided, in adding to the solution an excess of caustic potash, and in warming the whole; whereupon the alumina would be dissolved, but the magnesia would remain behind. Yet this method, notwithstanding its shortness, is not preferable to that previously described; and the reason is, that when a large quantity of magnesia is present, the separation of alumina by caustic potash is never complete. It is therefore always better to separate first the greater proportion of the magnesia from the alumina, and then to dissolve the alumina in potash. When, however, a very small quantity of magnesia is to be separated from a very large quantity of alumina, it is advisable to employ the second method of separation.

A third method of separating alumina from magnesia consists in adding to the solution of the two earths, previously diluted with water, a solution of bicarbonate of potash. A strong effervescence is thereby produced, the alumina is completely precipitated, and the magnesia remains dissolved. The precipitate is washed, and then, in general, is dried, ignited, and weighed. It has, however, been already observed, that it is more accurate, when alumina has been precipitated by a potash salt, to redissolve it in muriatic acid, and to precipitate it again by ammonia, or better, by carbonate of ammonia. When, therefore, the precipitated alumina has been sufficiently washed, the wet filter with the precipitate is laid in a glass, and dissolved in muriatic acid: the solution is filtered, the filter washed, the alumina again precipitated. —The solution of magnesia is evaporated to dryness, by which the bicarbonate of potash is converted into carbonate of potash. To complete the separation of the magnesia, the dry mass is then treated according to the directions which have already been given.

Separation from Lime.—The separation of alumina from lime is accompanied by no difficulties. The solution of both earths is supersaturated with caustic ammonia, by which alumina alone is precipitated. But in this operation there is a precautionary measure to be observed, through the neglect of which, in quantitative analyses, considerable errors can often take place. It is known, that caustic ammonia does not precipitate lime; yet when a solution containing lime is supersaturated with caustic ammonia, then, after a shorter or longer time, it absorbs carbonic acid from the atmosphere, and deposits sandy crystals of carbonate of lime on the sides of the glass. The more rapid or more dilatory production of these crystals depends upon the greater or smaller excess of ammonia which is present, and upon the concentrated or diluted state of the solution. When therefore the separation of alumina from lime is effected by caustic ammonia, the operator must carefully avoid a great excess of the latter; he must moreover, filter the precipitated alumina as quickly as possible, that it may not become contaminated by carbonate of lime; and, finally, must, during the filtration, keep the funnel covered with a glass plate, to prevent as much as possible the access of atmospherical air. The lime contained in the solution filtered from the alumina is precipitated by oxalate of ammonia. The ignited alumina is now weighed; after which it is moistened with water, and then tested with a little concentrated muriatic acid: if an effervescence ensue, the alumina is mingled with carbonate of lime.

Separation from Lime and Magnesia.—When alumina is to be separated from lime and magnesia, the operator commonly adds muriate of ammonia to the solution, and then precipitates the alumina by caustic ammònia. If the solution is very acid, the addition of muriate of ammonia is unnecessary, because a sufficient quantity of ammoniacal salt is produced by the supersaturation of the solution with ammonia. The precipitated alumina is quickly filtered, in order that it may not be contaminated by carbonate of lime. The lime is precipitated from the filtered solution by oxalate of ammonia. The solution filtered from the oxalate of lime contains the greater part of the magnesia, of which, however, a small quantity is retained by the precipitated alumina. To separate this portion, the alumina is, as has been explained above, dissolved in caustic potash, and the magnesia which remains undissolved in the potash is dissolved in muriatic acid, and added to the solution containing the principal quantity of magnesia. When the whole of the magnesia is together, it is precipitated by carbonate of potash, in the manner which has been already described.

A second method of effecting the separation of these earths, consists in adding to the solution, a solution of bicarbonate of potash, which precipitates the alumina alone, and retains the other earths in solution. The solution filtered from the precipitated alumina can be evaporated to dryness, and the dry mass treated with hot water; whereupon carbonate of lime and carbonate of magnesia remain undissolved. These two compounds are separated from one another, according to one of the methods described under Magnesium. In this case, however, the best method is to convert the two earths into sulphates, and to separate them by a solution of sulphate of lime.—Of this method of separating alumina from lime and magnesia it is to be moreover remarked, that it is capable of being employed with advantage only when the quantity of lime which is present is very small. The bicarbonate of potash converts the lime and magnesia into bicarbonates. The bicarbonate of magnesia is pretty easily soluble in water, but the bicarbonate of lime is, on the contrary, difficultly soluble. When therefore the quantity of lime is considerable, the operator should take care, before mixing the solution with bicarbonate of potash, to dilute it with a very large quantity of water; yet even when this precaution is taken, there is still occasion to fear that the precipitated alumina may contain bicarbonate of lime.

Separation from Strontian.—For separating alumina from strontian, caustic ammonia is employed, precisely as in separating alumina from lime. There are here again the same precautionary measures to be observed. The precipitated alumina must be quickly filtered, in order that it may not be contaminated by carbonate of strontian; for solutions of strontian, when they are mixed with caustic ammonia, absorb, like calcareous solutions under the same circumstances, carbonic acid from the atmosphere.

Separation from Barytes.—The separation of alumina from barytes is effected by sulphuric acid, by which the barytes is precipitated. From the solution which is filtered from the sulphate of barytes, the alumina is precipitated by ammonia, or still better by carbonate of ammonia.

Separation from the Fixed Alcalies.—The separation of alumina from the fixed alcalies is effected by ammonia or carbonate of ammonia, by which the alumina is precipitated. The filtered solution is evaporated to dryness, and the dry mass is ignited in a counterpoised platinum crucible; thereby the ammoniacal salt, produced by the combination of the ammonia with the acid with which the alumina was previously combined, is volatilized, and the fixed alcali remains behind, combined with the acid with which it existed in solution before its separation from the alumina. When the acid, with which the alumina and fixed alcali were combined, is sulphuric acid, it is necessary, during the ignition, to treat the alcaline sulphate with carbonate of ammonia, according to the instructions which have been given at page 6.

Separation from Magnesia, Lime, and a Fixed Alcali.—When alumina is to be separated from magnesia, lime, and a fixed alcali, which separations frequently occur, especially in mineral analyses, the operator adds to the solution of these substances, first muriate of ammonia, and then caustic ammonia, by which alumina and a little magnesia are precipitated. When the solution is very acid, the addition of muriate of ammonia is unnecessary. The solution is quickly filtered, that it may not be contaminated by carbonate of lime. The lime is precipitated from the filtered solution, by oxalate of ammonia. The small portion of magnesia, which was precipitated with the alumina, is then separated by a solution of caustic potash; it is dissolved in an acid, and the solution is added to the solution filtered from the oxalate of lime. This is evaporated to dryness, and the dry mass is ignited to drive away the ammoniacal salts; the operator then cautiously adds sulphuric acid, heats the whole, and, at last, gently ignites it. The sulphate of magnesia is then separated from the alcaline sulphate, by the process which has already been described at page 29.

Analysis of Corundum and Spinell.—Alumina occurs in nature, as corundum, in such a state of compactness, that it cannot be dissolved by acids. Not even when it has been ignited with carbonate of potash or soda, can it be attacked by acids. Many native compounds of alumina with certain bases, in which compounds the alumina plays the part of an acid, possess a similar degree of compactness. Such a compound is the mineral composed of alumina and magnesia, and which bears the name of Spinell. These can only be dissolved in acids, when they have previously been melted with caustic potash. The analysis of these compounds, with the help of caustic potash, requires to be conducted with much circumspection. The method of proceeding which must be observed, is the same as that employed in the treatment of certain siliceous compounds with caustic potash. As this procedure will hereafter, when we treat of the quantitative determination of silicic acid, be circumstantially described, it is unnecessary to speak of it here.

IX. GLUCINUM.

Precipitation of Glucina by Ammonia.—Glucina is completely precipitated from its solutions by caustic ammonia. The precipitate has much similarity with precipitated alumina. Like that substance, it is very voluminous, and contracts exceedingly during the drying.

Separation from Alumina.—In the separation of glucina from alumina, advantage is taken of the solubility of the former in carbonated alcalies, of which carbonate of ammonia is that which is employed. There are two methods of effecting the separation. According to the first method, the operator adds to the solution in which the glucina and alumina are contained, a concentrated solution of carbonate of ammonia; he then closes the vessel, and allows the whole to remain a pretty long time together, taking care to agitate the mixture frequently. It is necessary that the carbonate of ammonia be added in very considerable excess, because a small quantity of it precipitates the glucina, and the precipitate thus formed can only be gradually dissolved by a very great excess of the precipitant. It is consequently observed, after the addition of the excess of carbonate of ammonia, that the bulky precipitate gradually diminishes, as the precipitated glucina gradually dissolves. Thereupon the alumina is filtered, well washed, dried, ignited, and weighed. The solution, filtered from the alumina, is evaporated to dryness. The evaporation is performed in a porcelain capsule, or what is better, in a platinum capsule. In proportion as the carbonate of ammonia is volatilized, the glucina is precipitated, and the liquid becomes troubled. The dry mass consists of glucina, mingled with a salt which contains ammonia, combined with the acid which was previously combined with the glucina and alumina. The dry mass is ignited: thereupon the ammoniacal salt volatilizes, and glucina alone remains behind, and can be weighed.

The second method of separating glucina from alumina is as follows: Both earths are precipitated together by caustic ammonia. The voluminous and still moist precipitate is taken from the filter. The filter is treated with muriatic acid, and washed very clean. This solution and the moist precipitate are brought together into a flask, and digested a pretty long time with an excess of carbonate of ammonia, by which the glucina is gradually dissolved. The farther treatment is precisely the same as in the first method. When the operator has to separate glucina merely from alumina, the first method is preferable to the second; but on the contrary, the latter is employed in many cases where both earths are obliged to be precipitated together, in order that they may in this manner be separated from other substances.

Separation from Magnesia.—The separation of glucina from magnesia can be performed exactly in the same manner as the separation of alumina from magnesia; for glucina, like alumina, is easily soluble in a solution of caustic potash. The operator must employ the first process, described at page 31.

Separation from Alcaline Earths and Alcalies.—The separation of glucina from lime can also be effected in the same manner as the separation of alumina from lime, page 34. The same is to be said of the separation of glucina from strontian, barytes, and the fixed alcalies.

X. YTTRIUM.

Precipitation of Yttria by Alcalies.—Yttria can be precipitated from its solutions by caustic alcalies, and for this purpose caustic ammonia can, in most cases, be employed. Yet when yttria is dissolved in nitric acid, or still more in sulphuric acid, it is necessary to make use of caustic potash as the precipitant; because, in these cases, ammonia would precipitate, not pure yttria, but sub-salts of yttria. But even then it is almost impossible, according to WÖHLER (POGGENDORFF'S Annalen, Th. XIII. p. 581), to obtain the yttria quite free from sulphate of potash.

Separation from Earths and Alcalies.—Yttria is separated from alumina and glucina by heating the solution with caustic potash ley, by which the alumina and glucina are dissolved.—From magnesia, yttria is separated by caustic ammonia, the solution having been previously mingled with a large quantity of muriate of ammonia. The separation of yttria from lime, strontian, barytes, and the fixed alcalies, is effected in the same manner as the separation of alumina from those substances.

XI. CERIUM.

Precipitation by Alcalies.—The oxides of cerium can be precipitated from their solutions by caustic ammonia; but it is better to effect this precipitation by caustic potash, because ammonia, according to BERZELIUS, generally precipitates sub-salts. The precipitate is dried, ignited, and weighed. After ignition, it is invariably in the state of peroxide of cerium, even when, previous to the ignition, it was in the state of protoxide of cerium. When the substance under examination contained merely protoxide of cerium, the quantity of it must be reckoned from the weight of the peroxide obtained.

Separation from Yttria.—The oxides of cerium are separated from yttria, in company with which they very frequently occur, by the following process, described by **Berzelius**. The operator places in the solution which contains yttria, in company with one or both of the oxides of cerium, and whether the solution be acid or neutral, a crust of crystallised sulphate of potash, which must be deposited in such a manner as to project above the surface of the liquid, in order that all parts of the solution may become fully saturated with sulphate of potash. The oxides of cerium, as well as yttria, have the property of forming double salts with potash and sulphuric acid; of these salts, however, that formed by yttria is soluble, while those formed by the oxides of cerium are insoluble in a saturated solution of sulphate of potash. The precipitate thus produced is pulverulent, possessed of a white colour when it contains protoxide of cerium, but exhibiting a lemon-yellow colour when it contains peroxide of cerium. The precipitate is permitted to subside, and after twenty-four hours, when the solution is saturated with sulphate of potash, it is filtered. The precipitate is then washed with a concentrated solution of sulphate of potash. It is afterwards dissolved in boiling water, and precipitated by caustic potash. This reagent must be added somewhat in excess, and the whole must be digested with the assistance of heat: if this precaution is neglected, it is easy to obtain a precipitate contaminated by a sub-salt. When the precipitate has been washed, it is ignited, upon which it becomes of a cinnamon-brown colour, and is completely converted into peroxide of cerium, even if it previously consisted of protoxide of cerium. The solution, from which the oxides of cerium have been thus separated, contains still the double sulphate of potash and yttria. From this solution the yttria is precipitated by caustic potash.

Separation from Earths and Alcalies.—The oxides of cerium are separated from glucina, alumina, magnesia, lime, strontian, barytes, and the fixed alcalies, by the processes that are employed to separate yttria from those substances.

XII. ZIRCONIUM.

Precipitation of Zirconia.—Zirconia can be precipitated from its solutions by caustic ammonia, and by caustic potash; but the precipitates thrown down by the former very often consist only of sub-salts, and not of pure zirconia. The bulky precipitate is washed, and then cautiously ignited, during which the peculiar incandescence of the zirconia may be observed: it is afterwards weighed. When also the solution of a salt of zirconia is mingled with a solution of sulphate of potash, we obtain, according to Berzelius (Poggendorff's Annalen, Th. iv. p. 136), a precipitate of zirconia. If as much sulphate of potash, in crystals, as is sufficient to saturate the liquid be added, the greater part of the zirconia is precipitated: its perfect separation is effected when the acid in the solution is exactly neutralised by potash. There is formed hereby a subsulphate of zirconia, containing potash. This is partially soluble in pure water, and must on that account be washed with water which contains ammonia. The salt is subsequently boiled in a solution of caustic potash, whereupon the hydrate of zirconia remains in a state of purity undissolved. Zirconia can be separated by this process from many other substances.

Separation from Earths and Alcalies.—Zirconia, like the oxides of cerium, like yttria, and especially like glucina, is soluble in carbonated alcalies. It is also particularly soluble, according to Berzelius, in a solution of bicarbonate of potash, or bicarbonate of soda; nevertheless, zirconia, which has already been precipitated, dissolves very slowly in these solutions. When, however, a solution of zirconia is dropped into a solution of bicarbonate of potash, or bicarbonate of soda, this takes place very quickly. When the solution is boiled, then mingled with muriate of ammonia, and again boiled, the zirconia is precipitated. The explanation of this is as follows: a portion of the zirconia was dissolved in the excess of carbonic acid, and was consequently precipitated by the boiling. The other portion of the zirconia was dissolved in the simple carbonate of potash, and precipitated by the ammonia of the muriate of ammonia. Zirconia can, in this manner, be separated from alumina, as it can also from magnesia, lime, strontian, barytes, and the fixed alcalies. The method of separating it with accuracy from the oxides of cerium, from yttria, and from glucina, remains still to be discovered. According to BERZELIUS (POGGENDORFF'S Annalen, Th. III. p. 208), the best process with which chemists are yet acquainted, is the following: The boiling solution is mixed with sulphate of potash, by which the greater part of the zirconia is precipitated as a subsalt. The operator then adds to the solution, which is acid, a small quantity of ammonia, but not so much as to supersaturate the free acid, which would occasion the precipitation of the oxides of cerium, of yttria, and of glucina. The precipitated subsulphate of zirconia is washed with pure water, by which, however, a small quantity of it is redissolved. It is afterwards treated with caustic potash, in the manner which has been described above. From the solution which is filtered from the zirconia salt, the other substances are precipitated by the processes which have been already described.

XIII. MANGANESE.

Precipitation by Carbonate of Potash.—The protoxide of manganese can be precipitated by pretty nearly the same reagents that are employed to precipitate magnesia, a compound with which the protoxide of magnesia has many properties in common. The best precipitant of protoxide of manganese is, consequently, the carbonate of potash. There are, moreover, in the preeipitation of the protoxide of manganese by carbonate of potash, many of those precautionary measures to be observed, which, by the quantitative determination of magnesia, have been circumstantially described. The precipitation must be effected in a boiling solution: the best method is to add to the solution of the protoxide of manganese an excess of carbonate of potash; and, then, by a strong heat, to evaporate the whole to dryness. Hot water is afterwards poured over the dry mass, upon which carbonate of protoxide of manganese remains behind. This salt is quite insoluble in water, and on that account can be much more accurately washed than the carbonate of magnesia. The filtered solution, also, contains none of the carbonate of protoxide of manganese in solution. The carbonate of protoxide of manganese is, after washing, dried, ignited in a platinum crucible, and weighed. During the ignition it loses its carbonic acid, and is converted into the brown intermediate oxide of manganese (Manganoxyd-oxydul). This requires a pretty strong heat; a red heat is, however, sufficient. From the weight of this brown oxide, the quantity of protoxide, when the substance under examination contained the manganese in that state, is calculated.

If the solution, from which the protoxide of manganese is to be precipitated by carbonate of potash, contains considerable quantities of muriate of ammonia, or of other ammoniacal salts, the precipitation must be proceeded with, precisely like the precipitation of magnesia by carbonate of potash; and care must be taken to add the proper quantity of carbonate of potash, which is to be ascertained by the means already described.

Precipitation by Caustic Potash.—The protoxide of manganese is also, like magnesia, precipitated by caustic potash. The precipitate, which is protoxide of manganese, with water, appears white at first; but, upon the filter, during the washing, changes very soon in colour, in consequence of the absorption of oxygen, and becomes from the surface throughout, black. This precipitate is likewise convertible by a very strong heat into brown oxide of manganese. It is, however, in but few cases that caustic potash is employed to precipitate the protoxide of manganese; carbonate of potash is generally preferred.

Estimation as Sulphate of Manganese.—The protoxide of manganese, when contained in a solution from which no other substance is to be quantitatively separated, and in which no other fixed constituent is contained, can be estimated in the state of sulphate; yet, this method of determination does not answer so well with this substance as it does with magnesia. When sulphate of protoxide of manganese is ignited in contact with air, it loses a small portion of its acid; and thence it comes, that, after the ignition, a very small quantity of the salt is found to be insoluble in water. When, however, the sulphate of protoxide of manganese has been only feebly ignited, the quantity which is thus decomposed is very inconsiderable; and in a great number of cases, the quantity of protoxide of manganese may by this easy process be sufficiently well determined. As to the method of operating, it is exactly the same as that which has been described in the article Magnesium, page 23. It is proper, in this experiment, to avoid adding a very great excess of sulphuric acid, because it is difficult to expel such an excess of acid without, at the same time, expelling a portion of that which should remain behind.

Precipitation of Deutoxide of Manganese by Ammonia.—When manganese exists in solution in the state of deutoxide (Manganoxyd), which is but seldom the case, it can be precipitated by caustic ammonia. The precipitate of deutoxide of manganese thus obtained, can be converted by strong ignition into brown oxide of manganese. But as this requires a greater degree of heat than can be produced by a spirit lamp with circular wick, and as the operator cannot be quite sure that the deutoxide loses oxygen when a lower degree of heat is employed, it is better to convert the deutoxide into protoxide while in solution. The best method of performing this, is to add muriatic acid to the solution, and to warm the mixture; a disengagement of chlorine then takes place, and the deutoxide is converted into protoxide. It is improper to add sugar, gum, or other organic substances, instead of muriatic acid, to the solution, as some chemists have recommended; for, although it is true that such substances effect the conversion of the deutoxide into protoxide, yet the presence of non-volatile organic substances in the solution can, in a great number of cases, be productive of disadvantages, and even quite prevent the precipitation of many substances by means of alcalies. When, however, it may be desirable to convert the deutoxide into protoxide by such a method, the substance which should be taken, as being best adapted to the purpose, is alcohol.

Reduction of the higher Oxides of Manganese to the Brown Oxide by Ignition.—When the compound to be examined is deutoxide of manganese, which occurs in nature in a state of purity, and also in combination with water, or when it is peroxide of manganese or substances which contain it, the best method of proceeding, when no other fixed constituent than manganese is present, is to ignite the substance so long that it becomes completely converted into brown oxide of manganese. The loss of weight indicates the quantity of the oxygen expelled, provided no other volatile substance, as, for example, water, was contained in the compound. In what manner the weight of the water is to be estimated, will be explained farther on, under the head of Hydrogen.—The brown oxide of manganese (Manganoxyd-oxydul), is an oxide of manganese, which, according to the experiments of ARFVEDSON (*Afhandlingar i Fysik*, T. VI. p. 227), suffers no alteration on being exposed to a red heat. Protoxide of manganese, and carbonate of protoxide of manganese can be easily converted into brown oxide of manganese, by being strongly ignited in a platinum crucible over a spirit lamp with circular wick, provided the access of atmospheric air is not completely prevented. Deutoxide of manganese and peroxide of manganese, however, are changed into brown oxide of manganese only when exposed to a white heat; it is, therefore, necessary to ignite them in a furnace. They should be placed in a small counterpoised platinum crucible, and the latter should be enclosed in a larger earthen crucible.—But when the substance to be examined contains extraneous matters, it must be dissolved in muriatic acid, with the assistance of heat; and the foreign substances must be separated from the resulting solution.

Separation from Zirconia, the Oxides of Cerium, Yttria, and Glucina.—The separation of protoxide of manganese from zirconia, the oxides of cerium, from yttria and glucina, can be effected by the same operations that are employed to separate magnesia from these substances. The protoxide of manganese is not precipitated by ammonia, if the solution contains a large quantity of muriate of ammonia. The other substances, on the contrary, are precipitated under these circumstances. But hereby is the precautionary measure to be observed, of quickly filtering the precipitate; because the protoxide of manganese contained in the ammoniacal solution very soon becomes more highly oxidated, and precipitates in the state of deutoxide.

Separation from Alumina.—The protoxide of manganese can be separated from alumina also, in the same manner. Here, however, even when a large quantity of muriate of ammonia is contained in the solution, a small portion of protoxide of manganese is always precipitated with the alumina, by the caustic ammonia. This is discovered by the brownish colour which the precipitated alumina soon acquires on being exposed to the air. This is attributable to the conversion of the small quantity of protoxide of manganese into deutoxide, by the absorption of oxygen from the air. The precipitated alumina must, consequently, be again dissolved in caustic potash, upon which the deutoxide of manganese remains undissolved. Generally speaking, the operation is to be conducted in the same manner as the operation of separating magnesia from alumina, by means of caustic ammonia, which operation has been described above, at page 31.—Alumina can also be immediately separated from protoxide of manganese, by means of caustic potash; the solution of both substances is, with this view, to be gently boiled with an excess of caustic potash. When, however, a considerable quantity of ammoniacal salts is contained in the solution, it is better and more economical to decompose these by means of carbonate of potash, employed with heat.—By bicarbonate of potash, the protoxide of manganese cannot be separated from alumina, because the protoxide of manganese is dissolved by bicarbonate of potash in extremely small quantity.

Separation from Magnesia.—The separation of protoxide of manganese from magnesia is effected in the following manner: The solution of both substances is mingled with so much muriate of ammonia, that upon the subsequent addition of ammonia no precipitate is produced. If the solution is acid, it is unnecessary to add muriate of ammonia, because a sufficient quantity of an ammoniacal salt is produced by the saturation of the acid with ammonia.

The operator then adds a sufficient quantity of bihydrosulphuret of ammonia to precipitate all the protoxide of manganese in the state of sulphuret of manganese. It is not indispensable, in this case, that the bihydrosulphuret of ammonia should contain no free ammonia. The protoxide of manganese is precipitated as sulphuret of manganese, with a flesh red, or in large quantity, with more of a reddish colour. When the precipitate has entirely subsided, the solution is filtered. Were an attempt to filter the solution to be made, before the precipitate had completely fallen down, the solution would pass through the filter too slowly. The sulphuret of manganese is then edulcorated, not with pure water, but with water to which bihydrosulphuret of ammonia has been added. After edulcoration, the sulphuret of manganese, upon the filter, very soon changes its colour; it acquires oxygen, and becomes at the surface, first brown, and finally black. In the performance of this operation, it is absolutely necessary, on account of the rapid oxidising of the sulphuret of manganese, to filter and to wash the precipitate without interruption. It is, however, impossible to calculate the quantity of protoxide of manganese from the weight of the resulting sulphuret of manganese, since the latter has the property of becoming so quickly oxidised. The sulphuret, together with the wet filter, is therefore carefully placed in a glass, and muriatic acid is poured over it. There is then a disengagement of sulphuretted hydrogen gas. The glass is exposed to a very gentle heat, which is continued until the liquid no longer smells of sulphuretted hydrogen; the solution is thereupon filtered, and the protoxide of manganese is precipitated by carbonate of potash. The protoxide of manganese can also be converted into sulphate of protoxide of manganese, according to the instructions which have been given at page 43.—The solution filtered from the manganese contains the whole quantity of magnesia. It is first acidulated by muriatic acid, to decompose the excess of bihydrosulphuret of ammonia; and the solution is permitted to digest at a gentle heat until it no longer smells of sulphuretted hydrogen. The solution is then filtered for the purpose of separating the finely divided sulphur which has been deposited during the digestion;

after which, the quantity of the magnesia can be directly determined. It may be precipitated by carbonate of potash; or, what is better, can be converted into sulphate of magnesia.—Very often also are magnesia and protoxide of manganese precipitated together by carbonate of potash; then dissolved in muriatic acid, and separated in the manner which has been just described.

Another method of separating protoxide of manganese from magnesia, has been given by **STROMEYER** (**POGGENDORFF**'s Annalen, T. XI. p. 169). A current of chlorine gas is led through the liquid which contains both substances in solution. The solution of the substances is commonly effected in muriatic acid. In the cold, the passing of chlorine gas through the solution produces perchloride of manganese. A solution of bicarbonate of potash precipitates deutoxide of manganese from this solution, while magnesia remains dissolved. This can be afterwards obtained by evaporating the filtered solution by a strong heat to dryness. **STROMEYER** directs a solution of phosphate of soda, to which ammonia has been added, to be employed to precipitate the magnesia.

Separation from Lime.—The separation of protoxide of manganese from lime can be effected in two ways. If a very small quantity of protoxide of manganese is to be separated from a very large quantity of lime, the solution, which is previously to be pretty much diluted with water, is mixed with such a quantity of muriate of ammonia, that upon the addition of an excess of caustic ammonia, no precipitate is produced. If the solution is acid, the addition of muriate of ammonia is unnecessary. The lime is precipitated by oxalate of ammonia, and the whole is warmed, in order that the oxalate of lime may be very quickly filtered; for, if the filtration were to be performed after some time, the oxalate of lime would be contaminated by deutoxide of manganese, because the protoxide of manganese contained in the ammoniacal solution becomes more highly oxidised, and then precipitates.—From the solution filtered from the oxalate of lime, the protoxide of manganese is then either precipitated, or converted into sulphate of protoxide of manganese.

The method just described is, however, unavailable, when a large quantity of protoxide of manganese is to be separated from lime. For, in this case, it would not only be more difficult to prevent the contamination of the oxalate of lime by deutoxide of manganese, but also almost impossible to hinder the precipitation of a small quantity of oxalate of protoxide of manganese, in company with the oxalate of lime, especially if the solution were not exceedingly dilute. In this case, therefore, another process must be followed. The liquid is mixed with such a quantity of muriate of ammonia, that, upon the addition of caustic ammonia, no precipitate is produced. This addition of muriate of ammonia, however, is not required when the solution is very acid, because by the saturation of the excess of acid, a sufficient quantity of an ammoniacal salt is formed. The protoxide of manganese is then precipitated by bihydrosulphuret of ammonia, in the state of sulphuret of manganese. The precipitate, after having subsided for a short time, is quickly separated by filtration; both the funnel and the receiving vessel being carefully covered with glass plates, to prevent any contamination of the sulphuret of manganese by carbonate of lime. The best method of operating is to mix the solution with bihydrosulphuret of ammonia, in a flask which can be closed by a cork, in order that the sulphuret of manganese may have time to subside completely without being affected by the presence of atmospheric air. The sulphuret of manganese is immediately edulcorated with water, to which a little bihydrosulphuret of ammonia has been added. It is afterwards treated with muriatic acid, in the manner which has been described above. The solution, which is filtered from the sulphuret of manganese is acidulated by muriatic acid, that the excess of byhydrosulphuret of ammonia may be destroyed; and is exposed to a gentle heat until it no longer smells of sulphuretted hydrogen. This invariably occasions the precipitation of a small quantity of sulphur, which is separated from the solution by filtration. The solution is thereupon slightly supersaturated with ammonia, and the lime is precipitated by oxalate of ammonia.

Separation from Alumina, Magnesia, and Lime.—When alumina, magnesia, and lime are to be separated from protoxide of manganese, the method of proceeding is different, according as the quantity of protoxide of manganese is smaller or larger. In the first case, the solution is mingled with muriate of ammonia, which, however, is not necessary when it contains free acid. The alumina is thereupon precipitated by caustic ammonia, which, at the same time, always precipitates small quantities of magnesia and protoxide of manganese. During the filtration, the alumina is, as much as possible, protected against the access of atmospheric air, in order that it may not be contaminated by carbonate of lime. The lime is then precipitated from the filtered solution, by means of oxalate of ammonia. In order to separate from the alumina the small portions of magnesia and protoxide of manganese which it contains, it is treated with caustic potash, in the manner which has been described above. The small portions of protoxide of manganese and magnesia are dissolved in muriatic acid, and added to the solution filtered from the oxalate of lime. The protoxide of manganese is then separated from the magnesia, by the process which has been given above.

If, on the contrary, the quantity of protoxide of manganese is larger, then, after having precipitated the alumina in company with small portions of protoxide of manganese and magnesia, by means of ammonia, the operator filters the solution, and precipitates the manganese, as sulphuret of manganese, by bihydrosulphuret of ammonia. The solution is filtered from the sulphuret of manganese, acidulated by muriatic acid, and heated until it no longer smells of sulphuretted hydrogen. It is then filtered, and supersaturated with ammonia; after which, the lime is precipitated by oxalate of ammonia. The operator can add together the solution of the sulphuret of manganese, the muriatic acid solution of the small portions of magnesia and protoxide of manganese which were precipitated with the alumina, and afterwards separated by caustic potash; and, finally, the solution which is filtered from the oxalate of lime. The whole quantity of magnesia can then be sepadrate from the protoxide of manganese, since both exist together in this mixture. It is better, however, to precipitate the protoxide of manganese alone from the solution of the sulphuret of manganese, and the magnesia alone from the solution filtered from the oxalate of lime; after which, the small portions of protoxide of manganese and magnesia which have been separated from the alumina, can also be separated and quantitatively estimated.

Separation from Strontian.—Protoxide of manganese can be separated from strontian as follows: The operator adds to the solution of both substances, so much muriate of ammonia, that no precipitate is formed on the addition of ammonia; if the solution is acid, it is unnecessary to add muriate of ammonia, as the addition of caustic ammonia alone suffices; thereupon, the manganese is precipitated in the state of sulphuret of manganese. During the filtering of this precipitate, the access of atmospheric air must be prevented, or carbonate of strontian will be produced. The solution filtered from the sulphuret of manganese is then rendered acid, and filtered from the precipitated sulphur; after which, the strontian is separated. This method of analysis is better than that, according to which the strontian is precipitated by sulphuric acid, because the sulphate of strontian is not completely insoluble in water.

Separation from Barytes.—Protoxide of manganese is separated from barytes, exactly as magnesia is separated from barytes; that is to say, by means of sulphuric acid. Barytes, according to TURNER's Experiments (POGGENDORFF's Annalen, Th. XIV. p. 218), is contained in almost all manganese ores.

Separation from Fixed Alcalies.—The separation of the protoxide of manganese from the fixed alcalies is attended with no difficulties. The solution is rendered alcaline by ammonia, and the manganese is precipitated as sulphuret. The solution is filtered from the sulphuret of manganese, acidulated, warmed, and again filtered. The quantity of the alcali contained in the solution is then estimated in the manner which has been described above.

XIV. IRON.

Conversion of Protoxide of Iron into Peroxide.—The quantity of iron, whether it be contained in the substance to be examined as metallic iron, or as protoxide, peroxide, or intermediate black oxide, is estimated only as peroxide. When a compound contains metallic iron, protoxide, or black oxide, it is dissolved in nitric acid or in aqua regia; the iron then exists in the solution in the state of peroxide. When a solution contains protoxide or black oxide, it is mixed with a little nitric acid, and exposed to heat; upon which peroxide is produced. If the solution be very dilute, the complete oxidation is not effected until the solution has been concentrated by evaporation. When the quantity of protoxide is pretty considerable, the solution, after the addition of nitric acid, and after it has been properly warmed, becomes black, and almost opaque; but it deposits no precipitate, and very soon afterwards becomes clear: the operator may then rest assured that all the protoxide has been completely changed into peroxide. The black colour is owing to the presence of nitric oxide, which is produced by the decomposition of the nitric acid, and absorbed by the solution of undecomposed protoxide of iron.

Precipitation of Peroxide of Iron by Ammonia.—When a solution contains peroxide of iron only, the precipitation is effected by caustic ammonia. The peroxide of iron is most completely precipitated thereby. The precipitate is reddish brown, very bulky, and, like the precipitate afforded by alumina, shrinks together, in some degree, on the filter while being washed. On drying, however, it diminishes extremely in bulk, and forms a hard, glassy, blackish brown mass. If the solution is warmed after the precipitation of the peroxide, the precipitate becomes immediately both darker and more compact; after being dried, it is ignited. It is liable to decrepitate when heated; on which account, it is necessary to apply the heat very cautiously at first. The peroxide loses no oxygen by being ignited over the spirit lamp with a circular wick; the filter may even be burnt with the peroxide without causing the reduction of any portion of the latter, provided the proper current of air is produced.—From the weight of the peroxide, the quantity of metal, of protoxide, or of black oxide, which may have existed in the substance submitted to analysis, is ascertained by calculation.

Precipitation of Peroxide of Iron by Caustic Potash.—The peroxide of iron can also be completely precipitated by caustic potash. The precipitate, however, is very difficultly washed clean, and always retains a little potash, in consequence of which, the analysis appears to produce a slight excess of peroxide of iron. If, therefore, peroxide of iron has, in any case, been precipitated by caustic potash, the precipitate must, while still moist, be redissolved in muriatic acid, and precipitated afresh by caustic ammonia.

Precipitation of Peroxide of Iron by Carbonate of Potash or Ammonia.—The peroxide of iron is wholly precipitable by carbonate of potash or carbonate of ammonia, from a solution which is neutral. If the solution of peroxide of iron be acid, the bicarbonate of alcali which is produced, retains a portion of peroxide of iron in solution. This portion of peroxide is completely precipitated when the solution has, during a considerable time, been exposed to heat.

Precipitation of Iron by Bihydrosulphuret of Ammonia.—In a great number of cases, peroxide of iron is precipitated as sulphuret of iron, for the purpose of separating it from other substances. To this end, the solution, if it be acid, is neutralised by ammonia, of which a slight excess may be added. This excess produces, indeed, a precipitate of peroxide of iron, which, however, is not disadvantageous. The operator now adds bihydrosulphuret of ammonia until all the peroxide of iron is converted into sulphuret of iron. This sulphuret forms a bulky black precipitate which sinks very slowly. When the supernatant liquid has merely a yellow colour from the excess of bihydrosulphuret of ammonia, the solution is filtered, and the sulphuret of iron is immediately washed with water containing a little bihydrosulphuret of ammonia. Often, after the sulphuret of iron has fallen down, the supernatant solution exhibits a green colour. This colour arises from the presence of finely divided sulphuret of iron, which remains suspended in the solution, and does not subside till after a considerable time. If the solution be filtered, it passes green through the filter. To prevent this accident, it is only necessary to expose the green coloured liquid for a considerable time to a gentle heat on the sand bath; the sulphuret of iron then subsides, and the liquid becomes yellow. The sulphuret of iron upon the filter very soon becomes oxidised; its surface, after a short time, acquires a reddish colour, which is gradually communicated to the whole mass. This rapid oxidation of the sulphuret of iron renders it impossible to determine from its weight the quantity of peroxide of iron which is its equivalent; the sulphuret must, therefore, be converted into peroxide. The method of treatment is much the same as that employed with the precipitated sulphuret of manganese. The still moist sulphuret of iron is placed with the filter in a glass, and has muriatic acid poured over it; hereupon, sulphuretted hydrogen gas is disengaged, and the precipitate is dissolved. The solution is then exposed to a gentle heat, until it loses the smell of sulphuretted hydrogen. The operator now filters the solution, washes the filter accurately, adds nitric acid to the filtered liquid, and exposes it again to heat. The solution, previous to the addition of the nitric acid, contained the iron in the state of protoxide. By the joint agency of nitric acid and heat, the protoxide is converted into peroxide, which can then be precipitated by ammonia. The sulphuret of iron and the filter must not be treated directly with aqua regia, for the purpose of immediately converting the iron of the sulphuret into peroxide. The reason of this precaution is, that the action of aqua regia upon many sorts of paper produces certain organic substances which might partially hinder the precipitation of the peroxide of iron by ammonia. —When iron is to be precipitated as sulphuret, the state of oxidation in which the dissolved iron exists, is a matter of indifference. Protoxide of iron is precipitated by bihydrosulphuret of ammonia, with the same appearances as peroxide of iron. If the sulphuret of iron be strongly ignited, and the access of atmospherical air be not wholly restrained, it is possible thereby to convert it entirely into peroxide of iron. For this purpose, however, a stronger heat is required than can possibly be produced by the spirit lamp with circular wick. The oxidation can be easily effected in the muffle of a small cupellation furnace. The sulphuret of iron, with the filter, should be placed therein, in a small counterpoised platinum capsule or crucible.

Separation from Protoxide of Manganese by Alcaline Succinates.—The separation of peroxide of iron from protoxide of manganese, is performed as follows: Both oxides being dissolved in an acid, for example, in muriatic acid, the operator commences by adding muriate of ammonia to the solution; this is particularly necessary when the quantity of the protoxide of manganese is very considerable in comparison with that of the peroxide of iron. When, however, the liquid is very acid, the addition of muriate of ammonia is unnecessary, since the saturation of the acid with ammonia, in the next step of the operation, produces a sufficient quantity of an ammoniacal salt. The solution must then be very exactly saturated by ammonia. This exact saturation is a thing which it is very difficult to effect. It is particularly disagreeable when the quantity of protoxide of manganese is considerable. When the solution is pretty near the point of neutralisation, the ammonia must be added very cautiously; it is best to employ a solution of ammonia in a very large quantity of water. This diluted ammonia should be added to the saline solution in drops. It is known that a sufficient quantity has been added, when upon stirring the solution, the small quantity of peroxide of iron thrown down by the last drops of ammonia, does not redissolve. When this point is reached, the solution is placed in a situation where it is very slightly warmed; the small quantity of precipitated peroxide of iron then dissolves. A very small quantity of diluted ammonia is again added, the solution is again warmed, and thus the process is continued until a small quantity of peroxide of iron remains undissolved, and cannot be made to disappear by submitting the solution to the action of a very gentle heat. There being now a small quantity of peroxide of iron precipitated, it is essential that the supernatant liquid possess a red colour, and retain still the greater part of the peroxide of iron in solution. If, by the addition of too much ammonia, all the peroxide of iron has been precipitated, it is necessary to add to the solution a few drops of extremely weak muriatic acid, and to endeavour to redissolve all but a very small portion of the precipitated peroxide. The neutralisation having been thus effected, the operator must add to the solution, a solution of a neutral succinate, which produces an abundant cinnamon brown precipitate of succinate of peroxide of iron. This precipitate is much more bulky than that of peroxide of iron thrown down by ammonia. All the recited precautionary measures are necessary to avoid the precipitation of traces of manganese. When, before the addition of the alcaline succinate, a small portion of peroxide of iron is precipitated, while the greater portion is still kept in solution, the operator can be sure that no trace of protoxide of manganese is afterward precipitated with the peroxide of iron. If the solution has been previously saturated by ammonia, he cannot be sure that it is absolutely neutral; and when this is not the case, traces of succinate of peroxide of iron can afterwards remain in solution.

When, from the solution of a neutral persalt of iron, peroxide of iron is to be precipitated in the state of succinate, the neutral alcaline succinate can, of course, be applied immediately to the solution of the persalt of iron. When completely cold, the succinate of peroxide of iron is filtered, and edulcorated with cold water. Warm water cannot be used, because it decomposes the precipitate, and dissolves an acid succinate of iron. The operator may employ for these precipitations the crystallised succinate of soda, which can always be obtained in a state of neutrality. But, in general, the neutral succinate of ammonia is used; and, indeed, there are very many cases in which it is impossible to use any other succinate. It is not, however, the crystallised succinate of ammonia of which use is made, as that is an acid salt: the neutral succinate of ammonia is formed by the saturation of diluted ammonia with succinic acid. When the succinate of iron has been washed and dried, it is heated to redness. During the ignition, the operator must take particular care to support a current of air, lest the peroxide of iron be reduced by the charcoal of the succinic acid. To produce the current of air, a cold body is laid across the platinum crucible. With small quantities of succinate of iron, the reduction of the peroxide during the ignition can easily be prevented; but the prevention is more difficult with large quantities. It is possible, however, after the washing of the succinate of iron, to separate the greater part of its succinic acid. BERZELIUS directs us to pour diluted ammonia over the succinate of iron while still on the filter. Succinic acid is abstracted, and the precipitate becomes smaller in volume and deeper in colour.

From the solution filtered from the succinate of iron, the operator has still to separate the protoxide of manganese. It may either be precipitated by carbonate of potash as carbonate of manganese, or it may be converted into sulphate of manganese. In the latter case, however, the peroxide of iron must have been precipitated by succinate of ammonia, and not by succinate of soda.

Separation from Manganese by Ammonia.—The separation by alcaline succinates, of peroxide of iron from protoxide of manganese, has no difficulties, when there is a considerable proportion of peroxide of iron. But when the proportion of iron is small, it is found to be very difficult so to saturate the solution with ammonia that the greater part of the peroxide of iron shall remain in solution, and only a small portion be precipitated; because a single drop of very dilute ammonia is often sufficient to throw down the whole quantity of peroxide of iron. The difficulties of the process increase considerably when, at the same time, the quantity of protoxide of manganese is very considerable; for, in that case, the oxidising power of the air, exercised on the neutralised solution, can very easily produce a portion of peroxide of manganese, which, precipitating with the peroxide of iron, renders the result altogether inaccurate. When, therefore, a mere trace of peroxide of iron is to be separated from a very considerable quantity of protoxide of manganese, the best mode of proceeding is the following: The operator adds to the solution a large quantity of muriate of ammonia, and precipitates the peroxide of iron by caustic ammonia. When the solution is extremely acid, the addition of muriate of ammonia is unnecessary. An excess of ammonia is also to be avoided. The precipitated peroxide of iron is filtered as quickly as possible, lest it become contaminated with peroxide of manganese. Should the presence of manganese be still suspected in the peroxide of iron thus separated, the precipitate must be redissolved in muriatic acid, and the peroxide of iron be precipitated in the state of succinate. The peroxide of iron and the protoxide of manganese are thus easily and completely separated.

Precipitation by Alcaline Benzoates.—Instead of the succinates, we can, according to HISINGER (*Afhandlingar i Fysik*, T. III. p. 152), employ the benzoates with the like good consequences. Peroxide of iron is as perfectly precipitated by the one as by the other. And, by the precipitation with benzoates, the same precautionary measures are to be observed as by the precipitation with succinates. Formerly, when benzoic acid was cheaper than succinic acid, there was some advantage to be gained by using the former as a precipitant of the peroxide of iron. At present, however, the advantage, in point of economy, lies on the other side. There are other circumstances too, which render the employment of succinates preferable to that of benzoates. The precipitate of benzoate of iron is still more bulky than that of succinate of iron, and as the benzoic acid contains much more carbon than the succinic acid, there is still more occasion to dread the reducing effects of the subsequent ignition. Nevertheless, the operator has the same resource here that he had in the former case: he can separate the benzoic acid from the benzoate of iron, just as he could separate the succinic acid from the succinate of iron, that is to say, by caustic ammonia. In both cases, the addition of ammonia to the precipitate on the filter, effects the separation of *most* of the succinic acid, but never of the *whole*.

Separation from Zirconia.—To separate peroxide of iron from zirconia, the operator begins by adding to the diluted solution of the two oxides, a solution of tartaric acid. This acid has the property of rendering a great number of solutions of metallic oxides and earths, incapable of precipitation by alcalies; among other solutions, those of peroxide of iron and zirconia are thus affected. If, therefore, to the solution of these two bases, a sufficient quantity of tartaric acid has been added, the addition of an excess of ammonia produces no precipitate. The solution, then, being rendered ammoniacal, the operator gradually adds bihydrosulphuret of ammonia, as long as it produces a black precipitate. The peroxide of iron is hereby precipitated as sulphuret of iron, while the zirconia remains in solution. When the precipitate has completely subsided, and the supernatant fluid has a yellow colour, it is filtered; if, however, the solution after some time remains greenish, it must not be filtered until, by exposing the whole to a very gentle heat, the entire deposition of the precipitate is occasioned, and the solution is rendered yellow. The sulphuret of iron must be very quickly and completely washed with water containing a little bihydrosulphuret of ammonia. When the washing is finished, the precipitate must be converted into peroxide of iron, in the manner which has been described above. The solution filtered from the sulphuret of iron is evaporated to dryness, and the dry mass is ignited in a counterpoised platinum crucible. Atmospheric air must be permitted to have access, and the ignition must be continued until the zirconia becomes white. But it is somewhat difficult, when the quantity of the dry mass is rather considerable, to bring the ignition to this perfection, because the carbon of the tartaric acid burns away very slowly. The consumption of the charcoal is very easily effected, however, when the dry mass is placed in a little counterpoised platinum capsule, and the capsule is placed in the muffle of a small cupellation furnace. When the zirconia is burnt to whiteness, it is ready to be weighed.—If the tartaric acid employed in this operation contain any fixed constituents, such as lime, &c., the whole quantity of these is found, at the end of the experiment, mixed with the zirconia.

Separation from Cerium.—The separation of peroxide of iron from the oxides of cerium, is effected in the same way as its separation from yttria.

Separation from Yttria.—Peroxide of iron can be separated from yttria, by the process employed to separate it from zirconia. More generally, however, yttria has been separated from peroxide of iron, by the process which follows: The solution of both substances is saturated with ammonia, and the peroxide of iron is precipitated by succinate of ammonia. The solution is filtered from the succinate of iron, and the yttria is precipitated by the addition of more ammonia.

Separation from Glucina and Alumina.—Peroxide of iron is separated, both from glucina and alumina, by caustic potash. The solution is evaporated to a rather small volume, and then, in a capsule of porcelain, or still better, of platinum, is mixed with a solution of caustic potash, and is warmed or gently boiled. At first, all the oxides are precipitated, but if a sufficient quantity of caustic potash has been added, the alumina and glucina are redissolved. In proportion as the two earths dissolve, the undissolved remainder, which, in the end, consists of peroxide of iron alone, becomes more darkly brown in its colour. The operator filters the solution, and washes the peroxide of iron. He supersaturates the filtered liquor with muriatic acid, and then, if it contain alumina, he precipitates it with carbonate of ammonia; or, if it contain glucina, he precipitates it with caustic ammonia. Should both these earths be present, they must be separated in the manner which has been described at page 37. The peroxide of iron must, in the case of an accurate analysis, be redissolved in muriatic acid, and precipitated by caustic ammonia.—This method of separating the peroxide of iron from glucina and alumina has a very disagreeable attendant; it is, that an operator who is not very experienced, can never tell when the proper quantity of caustic potash is added to the solution. The dark brown colour of the undissolved peroxide of iron is a guide which often is deceptive. It is only when the solution of glucina or alumina in caustic potash has been filtered from the precipitated peroxide of iron, that the operator can ascertain whether the quantity of potash necessary to effect the complete separation of the substances has been added. The proof consists in adding to the filtered alcaline solution a few drops of muriatic acid. If this produces a small cloud of alumina or glucina, which, upon agitating the solution, is redissolved, it is a proof that the caustic potash has been added in sufficient excess.

Separation from Magnesia.—Peroxide of iron is separated from magnesia, nearly in the same way that it is separated from manganese. The operator first adds muriate of ammonia to the solution of iron and magnesia, and then applies an excess of caustic ammonia. If the solution be very acid, the addition of muriate of ammonia is unnecessary. The peroxide of iron thus precipitated is always accompanied by a little magnesia, even when the quantity of muriate of ammonia in the solution, is very considerable. The precipitate is dissolved in muriatic acid, the solution is accurately saturated with ammonia, and the peroxide of iron is precipitated by a neutral alcaline succinate, in the manner, and with all the precautions, which have been fully described at page 55. The solution filtered from the succinate of iron, as it contains a small quantity of magnesia, is to be added to the solution which was filtered from the peroxide of iron precipitated by ammonia, and which consequently contains the main quantity of magnesia. The magnesia is then precipitated from the mixed solution.

Separation from Lime and Strontian.—Peroxide of iron is separated from lime and strontian by caustic ammonia, which precipitates the oxide but not the earths. The solution is filtered from the peroxide of iron, and the earths are precipitated from the filtered solution. The operator has hereby to observe the precaution of very quickly filtering and washing the peroxide of iron; he has also to take care to protect the precipitate, during the filtration, as much as possible against the action of the air; the peroxide of iron can otherwise be easily contaminated by carbonate of lime, or of strontian.

Separation from Barytes.—Peroxide of iron is separated from barytes by sulphuric acid. The solution is filtered from the sulphate of barytes, and the peroxide of iron is precipitated by ammonia.

Separation from Fixed Alcalies.—Peroxide of iron is separated from the fixed alcalies by caustic ammonia. The solution filtered from the precipitated peroxide of iron contains the alcalies. By evaporating the solution and igniting the dry mass, the alcalies are obtained in combination with the acid which was contained in the solution of peroxide of iron and alcalies.

Separation from several of the preceding Substances.—When peroxide of iron is to be separated from several of the substances which have been spoken of above, the course of the analysis may be inferred from what has been said on the separation of each particular substance. When, for example, peroxide of iron is to be separated from protoxide of manganese, alumina, magnesia, lime, and a fixed alcali, the separating processes may be as follows: The operator adds to the solution a sufficient quantity of muriate of ammonia, which, however, is not necessary when the solution is very acid. He then supersaturates the solution with caustic ammonia. The precipitate which appears, is quickly filtered, and, during the filtration, is protected as much as possible from the atmosphere. The lime is precipitated from the filtered liquor by oxalate of ammonia. The precipitate resulting from the application of caustic ammonia, contains peroxide of iron and alumina, as well as small quantities of magnesia and protoxide of manganese. It is redissolved in muriatic acid, care being taken to avoid an excess of acid: the solution is then boiled with caustic potash. The alumina is dissolved by the potash, and is afterwards precipitated from the filtered solution, in the manner described at page 32. The caustic potash, which dissolves the alumina, precipitates the peroxide of iron with the small quantities of magnesia and protoxide of manganese. This precipitate is dissolved in muriatic acid, the solution is diluted with water and saturated with ammonia. The peroxide of iron is then precipitated by succinate of ammonia. The solution filtered from the succinate of iron is mixed with the solution filtered from the oxalate of lime; and by means of bihydrosulphuret of ammonia the protoxide of manganese is precipitated as sulphuret of manganese. The solution filtered from this precipitate, is acidulated by muriatic acid, and warmed, to destroy the excess of bihydrosulphuret of ammonia. It is filtered, and evaporated to dryness, and the dry mass is ignited. It is then treated with sulphuric acid, and is again evaporated to dryness. It is now once more ignited, and is treated, during the ignition, with dry carbonate of ammonia, to convert the alcaline bisulphates into neutral sulphates. When the ignition is ended, the saline mass is weighed. It contains the magnesian sulphate and the alcaline sulphate. The magnesia and the alcali are separated by the process described at page 29.—The course of this analysis is somewhat modified when the quantity of protoxide of manganese is very considerable. In that case, the greater portion of the protoxide of manganese is precipitated by bihydrosulphuret of ammonia, before the lime is precipitated by the oxalate of ammonia. The reason for this precaution is given at page 48.

Separation of Peroxide of Iron from Protoxide of Iron.—The separation of peroxide of iron from protoxide of iron is exceedingly difficult. When other substances are in combination with these oxides, the difficulties are much increased. And when the compound is incapable of solution in acids, the separate determination of the oxides cannot possibly be effected.

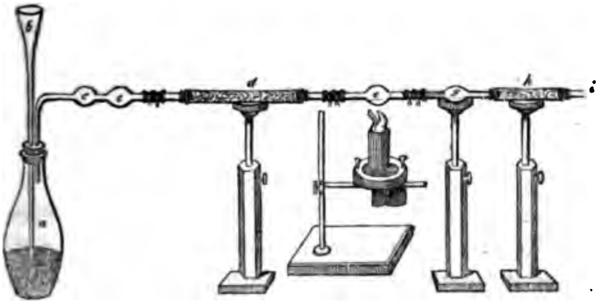
Let it be supposed that compounds are to be examined, which consist merely of peroxide and protoxide of iron, and which are soluble in acids. Compounds of this description are the native magnetic iron ore, and the sort of oxide of iron which is produced when iron is heated to redness in the open air (Eisen-Hammerschlag). A given quantity of the compound is dissolved in muriatic acid, nitric acid is added to the solution, and the whole is heated, to convert the protoxide of iron into peroxide. The solution is then diluted with water, and the peroxide of iron is precipitated by ammonia. The precipitate is washed, dried, ignited, and weighed. From the weight of the peroxide, it is easy to learn with how much oxygen the substance must have combined, that the protoxide of iron which it contained, might be converted into peroxide.

All the increase of weight which the mixture of oxides has experienced on being converted into peroxide, is owing to the acquisition of oxygen. The oxygen has combined with the protoxide of the compound, and is half so much in quantity as the oxygen previously existing in the protoxide; for the protoxide of iron, on being fully converted into peroxide, acquires one half more oxygen than it already possessed. Thus, then, finding first, the quantity of oxygen gained by the substance operated upon, we find next the quantity of oxygen belonging to the protoxide existing in the compound; and herefrom, it is easy to calculate the quantity of the protoxide. When this is found, the quantity of the peroxide contained in the substance is learned from the difference in weight, between the quantity of the compound submitted to analysis, and the quantity of protoxide made out by calculation.

It is easy to perceive that, in this analysis, the utmost degree of accuracy must be observed. In the compounds of peroxide of iron with protoxide of iron, the quantity of the former is generally very large in comparison with that of the latter; the increase of weight gained by the substance, when its protoxide is converted into peroxide, is therefore very small; and when even a very small error is committed in the determination of this increase of weight, this error becomes very considerable in the subsequent calculation of the quantity of protoxide.

When the substance submitted to analysis contains small quantities of constituents which are insoluble in muriatic acid, the solution is filtered from the insoluble remainder, and the weight of the latter is determined and deducted from that of the substance submitted to analysis. These insoluble constituents are almost always deposited, as well by the magnetic iron ore as by the different sorts of oxide produced by heating iron to redness in the open air.

Reduction of the Oxides of Iron by Hydrogen Gas.—The quantity of oxygen contained in a compound, consisting merely of protoxide and peroxide of iron, can be determined by following a method differing altogether from the above. This method consists in converting the oxides into metallic iron. The reduction is effected by passing a stream of dry hydrogen gas over the oxides, while exposed to heat. By the combination of the hydrogen gas with the oxygen of the oxides of iron, a certain quantity of water is produced, of which care is taken to determine the weight. The performance of the experiment is as follows: The operator produces the hydrogen gas in a flask *a*, which is closed by a cork, in which two holes are bored. Through one of these holes passes a funnel *b*, with a long neck; through the other hole passes a tube, which is bent at a right angle, and intended to lead away the gas. In this tube two bulbs *c c* are blown. In the flask *a* the operator puts some granulated zinc, and as much water as occupies one-third part of its capacity. The glass tube of the funnel *b* must pass below the surface of the water. Sulphuric acid is gradually poured through the funnel into the flask, so as to disengage a very slow current of hydrogen gas, which passes away by the conducting tube. A considerable portion of the vapour of water, which flies off with the hydrogen gas, is deposited in the two bulbs *c c*. The remainder of the vapour of water is completely separated from the hydrogen gas, by forcing the latter to pass through the glass tube *d*, which is filled with dry chloride of calcium, and connected by a tube of Indian rubber with the tube which leads the gas from the flask. The other end of the tube containing the chloride of calcium, is connected, likewise by a tube of Indian rubber, with a glass tube, having a bulb *e* blown



in the middle of it. It is necessary that the bulb *e* be of pretty strong glass, that it may not be injured or melted by the action of the heat applied to assist the decomposing power of the gas. Instead, therefore, of blowing a bulb in the middle of a glass tube for this purpose, it is better to take a little glass bulb, formed of strong glass, and to solder two small glass conducting tubes to its sides. The small glass tube, on that side of the bulb which is farthest from the tube holding the chloride of calcium, must be drawn out to a fine point. The bulb *e* and its two tubes being completed, it is first weighed alone with accuracy. So much of the substance to be analysed is then put into it as may be judged to be convenient; particular care being taken to lodge the whole portion in the bulb *e*, and to cleanse the glass tube at each side with the plume of a small feather. The bulb is then weighed again, and the increase of weight indicates the quantity of the substance submitted to analysis. It is proper, in most cases, to employ the substance in the state of powder, partly because it is then more easily decomposed by the hydrogen gas, but especially because it is then in the condition most adapted to avoid the loss which ensues when a substance, on the first application of heat, decrepitates, a phenomenon which very generally occurs with minerals. With the bulb *e*, a second bulb *g*, is, by means of an Indian rubber tube, so connected, that the point of the tube of the bulb *e* passes into the bulb *g*. The other glass tube of the bulb *g* is connected with the small tube *h*, which is filled with chloride of calcium, by means of a cork, which fits air-tight into the end of the tube *h*. The bulb *g*, the glass tube *h*, and the Indian rubber tube which connects *g* to *e*, are all to be weighed together, before they are joined to the rest of the apparatus.—When the apparatus is complete, and filled with hydrogen gas, the bulb *e* is very gradually heated; but afterwards the heat is slowly raised until the bulb becomes red-hot. The heat is applied by a spirit lamp with circular wick. By this operation, the oxides of iron are completely reduced to metallic iron. The water which is produced, drops from the pointed tube of the bulb *e* into the bulb *g*, where the greater portion remains in the liquid state. A smaller portion, which passes on in the state of vapour, is absorbed by the chloride of calcium in the tube *h*. Nothing escapes, therefore, by the tube *i*, but the superfluous dry hydrogen gas. When water ceases to be produced, which is the case when no new drops appear to form at the point of the tube in the bulb *g*, the decomposition is completed. The heat is then gradually diminished, and the whole is allowed to cool. During the cooling, a slow but continued current of hydrogen gas must pass through the apparatus. When the whole is perfectly cold, it is necessary to determine the weight of the iron which is formed in the bulb *e*, and the weight of the water which is produced by the operation. The greater part of the water is found in the bulb *g*; a smaller portion will have been absorbed by the chloride of calcium in the tube *h*. That these weighings may be properly executed, the bulbs *e* and *g* must be separated. The last drop of water that has been formed remains, however, in the end of the pointed tube of the bulb *e*. This water must not be weighed with *e*, but with *g*. For this reason, the pointed tube is cut off from the bulb *e* by means of a sharp file, and is allowed to remain with the bulb *g*. The tube *h*, the bulb *g*, the Indian rubber tube, and the point of the tube cut from the bulb *e*, can then be weighed together. The operator dries the piece of tube and weighs it alone. He weighs farther the bulb *e* without the piece of tube, and afterwards adds to this the weight of the latter. From these different weighings, it is easy to learn how much the substance which has been reduced by hydrogen gas, has lost in weight. This loss of weight consists of oxygen. The weight of the bulb *g* and the tube *h* at the end of the experiment, after allowing for the original weight of the apparatus and for the weight of the dry piece of pointed tube, gives the quantity of water produced. The quantity of oxygen essential to the constitution of this quantity of water, is then calculated. The oxygen indicated by the loss of weight suffered by the substance reduced, and the oxygen indicated by the quantity of water produced, are quantities which should be in exact accordance. Any difference which may be found, indicates inaccuracy in the performance of the operation.

It would be easy, in this experiment, to determine merely the weight of the reduced iron in the bulb *e*, and in verity, the whole apparatus would be much simpler, if the operator chose to dispense with the weighing of the water. But as the result of this experiment ought to be exceedingly exact, if it is intended to draw conclusions from it respecting the relative quantities of protoxide and peroxide of iron contained in the substance submitted to analysis, it is improper to neglect any means of confirming the result. Now the determination of the quantity of water formed, affords a very good confirmation of the quantity of oxygen lost by the substance when treated with hydrogen gas. It would be possible, with a view to another simplification of the apparatus, to omit the bulb *g*, and to allow the whole of the water produced to be absorbed by the chloride of calcium in the tube *h*. Thereby, however, the determination of the quantity of water, would come to be very inaccurate; the determination indeed could only be effected at all, when the quantity of water was very small. If the quantity of water was considerable, it would dissolve a portion of the chloride of calcium; the solution so produced would flow towards the point *i*, and a portion of water could be lost by dissipation in vapour. In many cases, it is also of importance to examine the nature of the water which is produced. The operator must invariably observe whether or not the water have any effect on litmus paper; it often can change the colour to red or to blue. When the water possesses any such property, it indicates that the oxides of iron submitted to analysis, were not quite free from foreign admixture.—Another precautionary measure to be observed in this experiment, is to apply to the bulb *e* the strongest degree of heat which the glass is capable of supporting. If a gentler heat is employed, it is indeed possible that the peroxide of iron may still be completely reduced, but the reduced iron may then have the pyrophoric property of entering into combustion when it comes into contact with atmospheric air. The farther precaution is also to be taken, of permitting the current of hydrogen gas to pass through very slowly, in order, not only that the whole of the water produced may be condensed in the vessels *g* and *h*, but also that all the vapour which the gas contains when it issues from the flask *a*, may be completely absorbed by the chloride of calcium in the tube *d*.

When the substance contains other oxides, which are irreducible by hydrogen gas, these are found at the end of the experiment, upon dissolving the result in muriatic acid. There often remain then small portions of foreign constituents, which are insoluble in muriatic acid. The weight of the insoluble matters is determined, and deducted from the weight of the substance submitted to analysis.

What is determined, by this experiment, is merely the quantity of the oxygen contained in a compound of peroxide and protoxide of iron. There are, however, methods of determining, with respect to such compounds, the quantity both of peroxide and protoxide. These methods can even be often employed, when the two oxides of iron are combined with other substances. But in all cases, it is necessary that the substance to be analysed be soluble in muriatic acid.

Experimental Determination of the Quantity of Peroxide of Iron, in a Compound of Peroxide and Protoxide.—The following method is employed to determine the quantity of peroxide of iron: An accurately weighed portion of the substance is placed in a capacious flask, which can be closed air-tight by a glass stopple. The substance may be employed in lumps, provided that the lumps can be dissolved by muriatic acid. If that is not the case, the substance must be pulverised before it is weighed. The flask is then filled with carbonic acid gas, by passing the gas through a glass tube, which goes nearly to the bottom of the flask, but does not touch the substance contained in the flask. When it is thought that the more ponderous carbonic acid gas has expelled all the atmospherical air from the flask, the glass tube is removed, the quantity of muriatic acid necessary to effect the solution of the substance is immediately added, and the flask is quickly closed. For the sake of greater certainty, a piece of wet pig's bladder is bound over the neck of the flask. When the solution of the substance is completely effected, the flask is opened and filled with liquid sulphuretted hydrogen. This solution of sulphuretted hydrogen must have been recently and expressly prepared for the occasion. It must be as completely saturated with gas as possible, must be perfectly clear, and completely free from separated sulphur. The flask being filled with this solution, must be immediately closed with the stopple, and again bound with pig's bladder, to prevent the access of air. The mixture becomes milky, but after the lapse of some days, sulphur is deposited, and the liquor becomes clear. The hydrogen of the sulphuretted hydrogen reduces the peroxide of iron, contained in the solution, to the state of protoxide of iron, sulphur being precipitated. If the solution be not rendered milky by the addition of the liquid sulphuretted hydrogen, and if no deposition of pure sulphur take place, then the substance contains merely protoxide and no peroxide of iron.—If there be a deposition of sulphur, the clear liquid is filtered as rapidly as possible through a small weighed filter, and the sulphur is then brought upon it to be edulcorated. During the filtration, the access of atmospheric air must be hindered as much as possible, that the undecomposed sulphuretted hydrogen may not be made to deposit an additional quantity of sulphur. When the washing is completed, the sulphur is dried on the filter by the application of a very gentle heat, and is then weighed. After the weighing, it is burnt, for the purpose of finding whether it be pure or not. If the substance submitted to analysis contained foreign bodies, insoluble in muriatic acid, these are obtained after the burning away of the sulphur. This remainder is weighed, and deducted from the weight of the sulphur. From the weight of the sulphur, it is easy to find the quantity of oxygen which has combined and formed water with the hydrogen of the decomposed sulphuretted hydrogen. This oxygen, in combination with iron, formed peroxide of iron, which has, by the operation of the sulphuretted hydrogen, been converted into protoxide of iron. If we take three times this quantity of oxygen, we have the whole quantity of oxygen which, in the original substance, was combined with iron into peroxide of iron. The quantity of the peroxide is therefore easy of discovery.—It is necessary to observe here, that a suitable quantity of the liquid sulphuretted hydrogen must be employed. Upon opening the flask, the liquid it contains must smell distinctly of sulphuretted hydrogen. If this be not the case, then the quantity of peroxide of iron in the solution, was too great in comparison with the quantity of liquid sulphuretted hydrogen.

Determination of the Quantity of Protoxide of Iron, in a Compound of Peroxide and Protoxide.—The method of determining the quantity of the protoxide of iron contained in the substance analysed, is as follows:—A weighed portion of the substance is dissolved in muriatic acid. This is done in the same manner as in the preceding case. The flask, in which the solution is made, must be one which can be securely closed by a glass stopple, only it need not be so large as the flask which is employed when the quantity of the peroxide is to be determined. It must, as above described, be filled with carbonic acid gas before the muriatic acid is added. When the solution of the substance is effected, the operator must quickly pour into the flask a solution of the double chloride of gold and potassium, or of gold and sodium, and close the flask. By the mutual action of these solutions, metallic gold is precipitated, and a corresponding proportion of protoxide of iron is converted into peroxide. If no gold is reduced, the substance contains no protoxide of iron. A still easier method of convincing oneself whether protoxide of iron be present or not, is to add to another solution of the substance, a solution of the red prussiate of potash, which detects, by the production of a blue precipitate, the slightest traces of protoxide of iron in solution. This blue precipitate is produced even when the protoxide is accompanied by a large quantity of peroxide of iron.—But if, now, metallic gold should have separated, it is, after some time, to be filtered. It is then to be washed well, gently ignited, and weighed. From the quantity of gold obtained, the quantity of oxygen which was necessary to convert the protoxide of iron into peroxide of iron is ascertained by calculation: this is the third part of the quantity of oxygen contained in the peroxide of iron which has resulted from the oxidation of the protoxide of iron. If we double this quantity of oxygen, we have the quantity of oxygen appertaining to the protoxide of iron contained in the substance analysed. Hence, the quantity of protoxide of iron can be easily calculated.—It is necessary that, during the solution of the substance in muriatic acid, the access of atmospheric air be prevented as much as possible, otherwise a portion of the protoxide might be converted into peroxide, before the addition of the gold solution.—One cannot, instead of a solution of the double chloride of gold and potassium, or of gold and sodium, employ a solution of the simple chloride of gold, with the like good consequences. Even when the latter is prepared with the greatest care, it yields reduced gold, in consequence of accidental circumstances, much easier than the crystallised double chloride of gold and potassium, or of gold and sodium does: the employment of the chloride of gold solution leads therefore to uncertain results.—If the substance submitted to analysis contain small portions of foreign admixtures, which are insoluble in muriatic acid, the reduced gold is dissolved in aqua regia, and thus separated from the impurities. The gold solution is filtered, and the insoluble substances are washed, dried, ignited, and weighed. Upon deducting the weight so obtained from that of the reduced gold, the remainder indicates the true quantity of the latter.

This method of determining the quantity of the protoxide of iron in a compound, can be employed in many cases, in which the above method of determining the quantity of the peroxide of iron is impracticable. It is easy to perceive, that it is impossible to execute the latter process, when the substance to be analysed contains constituents which sulphuretted hydrogen precipitates.

It has already been observed, that none of these methods can be employed when the substance to be analysed is insoluble in muriatic acid. Not only are we, in this case, without the means of determining the relative quantities of peroxide and protoxide of iron contained in the compound which is examined, but we are often unable to determine with certainty which of the oxides it is that a particular substance contains. We determine, in such cases, the quantity of iron as peroxide, and it is in general assumed, that, when no excess is obtained, by the analysis, the iron was contained in the substance as peroxide, and that, when an excess is obtained, it indicates the presence of protoxide. When the analysis has been executed with care, this assumption is proper enough if iron is the principal constituent of the substance examined. But if this is not the case, the hope of determining the state of oxidation of the iron, by experiment, must be given up. Even when the other oxides which the substance contains are incapable of reduction by hydrogen gas, we are still unable to determine the quantity of oxygen in the oxides of iron; because, in general, the oxides of iron, which are contained in substances that are insoluble in muriatic acid, are incapable of being reduced by a stream of hydrogen gas.—The colour of the substance, to which we might look as a means of indicating the state of oxidation of the iron it contains, is often very deceptive; yet, in general, it is considered that a green or black colour indicates protoxide of iron, while a red, yellow, or white colour authorises us to decide that peroxide of iron is present. It is indeed true that a green or black colour, especially when the substance acts strongly upon the magnet, is indicative of the presence of protoxide of iron. It is, however, no less true, that the substance can, at the same time, contain much peroxide of iron.

XV. ZINC.

Quantitative Estimation as Sulphate of Zinc.—When oxide of zinc is contained alone in a solution, and is to be quantitatively determined, it can be converted into a sulphate, yet this method of estimation does not succeed so well as it does with magnesia. The sulphate of zinc loses a portion of its acid during ignition, on which account a small quantity of the salt is subsequently insoluble in water.

Precipitation by Carbonate of Potash.—The common precipitant of oxide of zinc is a solution of carbonate of potash. If the solution of oxide of zinc contain no ammoniacal salts, it is mingled with an excess of carbonate of potash, and heated till it boils: the precipitated carbonate of zinc is then filtered and washed. If, on the contrary, ammoniacal salts be present in the solution, the ammoniacal salts must first be destroyed by the joint operation of carbonate of potash and heat. The best method of proceeding, is to mix the solution with such a quantity of carbonate of potash, as may be sufficient to decompose the ammoniacal salts, and then to evaporate the mixture to dryness. Hot water is poured over the dry mass, the mixture is heated till it boils; the carbonate of zinc is then filtered. Care must be taken not to make a mistake in the quantity of carbonate of potash. The same general precautionary measures are to be observed, as have been described at page 25, in treating of the separation of magnesia from a solution containing ammonia. If a solution, containing oxide of zinc, were to be mixed with an excess of carbonate of potash, evaporated very slowly by a gentle heat to dryness, afterwards mingled with cold water, and then filtered to separate the carbonate of zinc, the liquid, which would pass through the filter, would still contain much oxide of zinc in solution; but this is not the case when the solution is evaporated by a strong heat, and the dry mass is treated with hot water, in the manner which has been recommended above.

After the precipitation of oxide of zinc by carbonate of potash, the operator should never neglect to examine whether the solution, filtered from the carbonate of zinc, is free from oxide of zinc. The best method of making this examination, is to add to the solution a few drops of bihydrosulphuret of ammonia. If a white voluminous precipitate is produced, it is a proof of the presence of dissolved oxide of zinc. The small quantity of sulphuret of zinc thus precipitated is, in such a case, to be treated in the manner which will be presently described.—When the carbonate of zinc has been precipitated with the requisite precautions, the quantity of sulphuret of zinc obtained from the filtered solution, is imponderable.

The carbonate of zinc is dried, and then strongly ignited in a platinum crucible over a spirit lamp with circular wick, by which means it is deprived of its carbonic acid. It is then weighed.

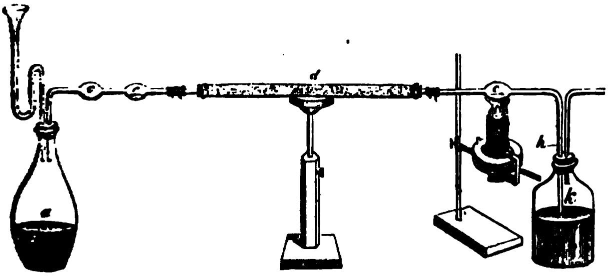
Precipitation by Bihydrosulphuret of Ammonia.—Zinc is often precipitated as sulphuret of zinc, by bihydrosulphuret of ammonia. If the solution of the zinc oxide salt be neutral, the bihydrosulphuret of ammonia is added to it directly; if the solution be acid, it is previously supersaturated with ammonia, by which, when the proper quantity is added, the oxide of zinc, at first precipitated, is redissolved; the operator can then precipitate the sulphuret of zinc, which is insoluble in every excess of alcali. The sulphuret of zinc forms a white voluminous precipitate, which must be allowed to subside completely before the solution is filtered. The operator first filters the clear solution, and brings the sulphuret of zinc upon the filter afterwards. If he neglect this precaution, the sulphuret of zinc stops the pores of the paper at the beginning of the filtering, and the solution passes through exceedingly slow. The sulphuret of zinc is washed with water, to which bihydrosulphuret of ammonia has been added: it is taken wet from the funnel, and digested, with the filter, in concentrated muriatic acid, by which it is dissolved, while a disengagement of sulphuretted hydrogen gas takes place. When the digestion has continued so long that the smell of sulphuretted hydrogen is scarcely any longer sensible, the solution is filtered, and the zinc is precipitated by carbonate of potash.

Separation from the Oxides of Iron.—Oxide of zinc is separated from peroxide of iron by caustic ammonia, which must be added in excess to the solution of the two oxides. The oxide of zinc remains in solution, while the peroxide of iron precipitates. From the solution, filtered from the peroxide of iron, the oxide of zinc is separated by mixture with carbonate of potash, and evaporation to dryness.—When oxide of zinc is to be separated from protoxide of iron, the latter must first be converted into peroxide of iron, by being heated with nitric acid.

The separation of oxide of zinc from peroxide of iron, by an excess of caustic ammonia, can only be effected with accuracy when the quantity of oxide of zinc is not very considerable. When, on the contrary, the oxide of zinc preponderates, it is difficult to obtain the peroxide of iron uncontaminated by oxide of zinc. It is, in that case, better to effect the separation of the two oxides by succinate of ammonia. The solution must first be saturated, or rather somewhat supersaturated by ammonia; a very small portion of the peroxide of iron must have been precipitated by the excess of ammonia, and must still remain undissolved when the succinate of ammonia is added.

Separation from Protoxide of Manganese.—From protoxide of manganese, the oxide of zinc cannot be separated by caustic potash. Even when a great excess of caustic potash is added to the solution of the two oxides, and the mixture is boiled for a considerable time, a good separation is not effected. On account of the access of air, the protoxide of manganese is partly converted into deutoxide, which can be separated by filtration, and cleansed by washing; there still remains, however, a small quantity of oxide of zinc, combined with the manganese, and the two substances cannot be totally separated by the action of caustic potash.

Manganese and zinc must, therefore, be separated in quite a different manner. The operator can precipitate them together, by carbonate of potash, as carbonated oxides, and afterwards convert them into metallic chlorides. The chloride of zinc is volatile, and can be separated from the chloride of manganese by distillation. The mode of proceeding is as follows: The carbonated oxides are strongly ignited, and weighed. During the ignition, they lose their carbonic acid. What remains is oxide of zinc, and brown oxide of manganese. This remainder is put into a little glass bulb, to each side of which a glass tube is soldered. These tubes must not be of too small a diameter, and one of them must be more than twice as long as the other. The bulb with its glass tubes is weighed, before the oxides are put into it. The weighing having been effected, the necessary quantity of the oxides is inserted, and the interior of the tubes is cleansed from any portion of the oxides by means of the plume of a feather. Thereupon the little apparatus is again weighed. This second weighing shows how much of the oxides is employed in the experiment. The operator now leads over these oxides a current of dry muriatic acid gas, disengaging it from the flask *a*, in which, previous to placing the apparatus together, a quantity of common salt has



been put. The opening of the flask *a* is closed with a cork, through which passes the neck of a long funnel, bent into a tube of safety, and of which the inferior end (which is best if pointed) goes but a few inches into the flask. Upon gradually pouring concentrated sulphuric acid through this funnel into the flask, a disengagement of muriatic acid gas is occasioned. This gas escapes through the gas-conducting tube, which, as well as the funnel, passes through the cork of the flask. This tube is bent at a right angle, and provided with two glass bulbs *c c*, in which the greater portion of the moisture is condensed. To dry the gas completely, it is next passed through the glass tube *d*, which is filled with chloride of calcium, and connected with the gas-conducting tube by a tube of Indian rubber. The other end of the tube containing the chloride of calcium, is connected, also by means of a tube of Indian rubber, with the bulb *e*, in which the oxides for decomposition are placed. The longer of the two glass tubes, with which the bulb *e* was provided, must have been bent, by heating it over the flame of a spirit lamp with circular wick, once, at a right angle. This bending must have been effected after the second weighing of the bulb, for had the bend been made in the tube before the oxides had been inserted in the bulb, the weighing of the bulb with the oxides would have been difficult. The tube, thus bent at a right angle, passes through a cork which closes the mouth of the flask *k*. This vessel is half filled with water, mixed with caustic ammonia. The glass tube ends just below the surface of the liquid. The cork of the flask *k* has a second hole, through which another gas-conducting tube passes.—When, now, the atmospheric air has been expelled from the apparatus by the stream of muriatic acid gas, the bulb *e* is gradually heated by the flame of a spirit lamp with circular wick. The oxides are thereby converted into metallic chlorides; the conversion, however, takes place but slowly. The chloride of zinc volatilizes, yet its complete separation by volatilization, is effected only by the strongest degree of heat which the spirit lamp with circular wick can produce. If the quantity of chloride of zinc be considerable, the operation must be continued for several hours, before the whole of the chloride of zinc is distilled off. It is necessary that the glass tube, which is bent at a right angle, have a pretty large diameter, about the third of an inch, for example, in order that it may not be stopped up by the volatilized chloride of zinc. The flame of a small spirit lamp is employed to drive chloride of zinc from the bulb *e* towards the flask *k*. If it gather together in the bend of the tube, it is best driven on, by directing the flame of the spirit lamp towards that part of the tube with a blow pipe. The chloride of zinc is thus forced to pass into the flask *k*, by the solution in which it is dissolved. When no more chloride of zinc passes from the bulb *e* towards the flask, the experiment is finished. The flame of the lamp is then gradually diminished, and the bulb is allowed to cool, a continued current of muriatic acid gas being allowed to pass through the apparatus during the whole time of cooling. When the whole is completely cold, the glass tube is cut, with the help of a sharp file at the mark *h*. But if the chloride of zinc has not been driven beyond that mark, and cannot be readily driven so far, the tube is cut at a short distance from the bulb *e*, and the chloride of zinc which remains in the tube is very carefully washed into the flask *k*. The solution in the flask then contains all the zinc, which, at the beginning of the process, was contained in the bulb *e*, in the state of oxide. The operator adds to this solution, a sufficient quantity of carbonate of potash, and precipitates the zinc in the manner which has been described above. Thereupon, the portion of the glass tube in which the chloride of zinc was contained, is cleansed and dried; after which, the bulb *e* is weighed, and the chloride of manganese which it contains is separated from it by solution. The bulb is then dried, and again weighed, to enable the operator to determine, from the loss of weight, the quantity of the chloride of manganese. But as the glass is often attacked in this operation, and the chloride of manganese cannot, on that account, be fully dissolved, it is not possible to obtain thus a very accurate result. For this reason, when the chloride of manganese has been dissolved in water, it is proper to wash out the bulb *e* with diluted muriatic acid, and after that, with water; and to add the washings to the dissolved chloride of manganese, with which they form a clear solution. If a very small quantity of silicic acid, resulting from the decomposition of the glass, appear in the solution, it must be filtered. From the filtered solution, the protoxide of manganese is separated by carbonate of potash, in the manner which has been circumstantially described at page 42. The carbonate of protoxide of manganese is converted, by ignition, into brown oxide of manganese. The weight of the brown oxide of manganese, added to the weight of the oxide of zinc obtained, must agree with the common weight of the portion of the oxides employed in the experiment. When the relative proportions of the two oxides are thus learned by experiment, in operating upon a given portion, the operator is enabled to calculate the total quantity of each, contained in the substance submitted to analysis. As the bringing of the mixed oxides into the bulb *e* of the above-described apparatus, and the subsequent cleansing of the glass tubes, must necessarily be attended with some loss, it is impossible to obtain the whole of either oxide in an isolated state; but the weight of the mixed oxides, and the relative proportions being known, the total quantity of each oxide is easily found by calculation.

It might appear to be a better method to dissolve the carbonated oxides directly in muriatic acid; to convert them, by cautiously evaporating the solution to dryness, into chlorides, and afterwards to expose these chlorides in the apparatus, to heat and muriatic acid gas. Much time would be saved by proceeding in this manner, since the oxides are but slowly converted into chlorides by the passing over them of a stream of muriatic acid gas. This mode of proceeding, however, whatever advantages it may appear to present, is not one which can be recommended. The reason is, that it is impossible to weigh and to bring into the bulb *e*, the chlorides of zinc and manganese, with so much accuracy as the oxides.

Separation from Zirconia, the Oxides of Cerium, Yttria, and Glucina.—The separation of oxide of zinc from zirconia, the oxides of cerium, yttria, and glucina, could be effected by caustic ammonia, added in excess. Oxide of zinc would remain in solution, and all the other substances be precipitated. It is unknown, however, whether this method yields accurate results.

Separation from Alumina.—Oxide of zinc can be separated from alumina by caustic ammonia, when both oxides are dissolved in a liquid. There is, however, a native compound of oxide of zinc and alumina, called Gahnite, which is insoluble in acids. This mineral withstands even the action of carbonate of potash in a state of igneous fusion, and can only be rendered soluble in acids by fusion with caustic potash. The treatment of this substance by caustic potash is managed in the same manner as the treatment of certain siliceous substances by caustic potash. The peculiarities of this operation will be fully described in a subsequent section, when we come to speak of the analysis of siliceous substances.

Separation from Magnesia.—Oxide of zinc is separated from magnesia pretty nearly in the same manner that protoxide of manganese is separated from magnesia. So much muriate of ammonia is added to the solution, that upon the addition of caustic ammonia, both the oxide of zinc and the magnesia remain in solution. When the solution is acid, the addition of muriate of ammonia is unnecessary, because the saturation of the acid by ammonia produces a sufficient quantity of an ammoniacal salt. The zinc is precipitated from the ammoniacal solution by bihydrosulphuret of ammonia, as sulphuret of zinc. The solution, filtered from the sulphuret of zinc, is acidulated, warmed, and filtered from the sulphur. The magnesia can then be precipitated in the usual manner.

Separation from Lime.—The separation of oxide of zinc from lime can be effected in the same manner as the separation of lime from magnesia. The solution is made ammoniacal, and the lime is precipitated by oxalate of ammonia. The oxalate of zinc does not precipitate, being retained in solution by the ammonia. The solution, filtered from the oxalate of lime, is mingled with carbonate of potash, and evaporated by a strong heat to dryness. The oxide of zinc is thus obtained in the state of carbonate.—The operator can also separate lime from oxide of zinc, by adding ammonia to the solution, and precipitating the zinc as sulphuret of zinc, by bihydrosulphuret of ammonia. This precipitate must, however, be quickly filtered, and protected during the filtering, as much as possible, from atmospheric air, otherwise the sulphuret of zinc may be contaminated by carbonate of lime. But as, in this process, the precipitated sulphuret of zinc cannot be allowed to subside, it is good to effect the precipitation in a flask, which can be closed by a cork: the air can then be kept off, and at the same time, the precipitate be allowed to subside. When the sulphuret of zinc has fully subsided, the solution is filtered. The filtered solution is acidulated, warmed, and again filtered, to separate the sulphur. The operator can then precipitate the lime.

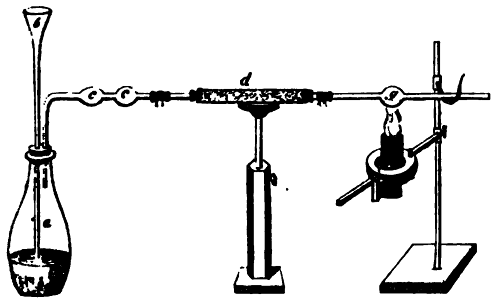
Separation from Strontian and Barytes.—Oxide of zinc can be best separated from strontian by the process which has just been described.—From barytes, on the contrary, oxide of zinc is separated by adding sulphuric acid to the solution, which throws down sulphate of barytes. The oxide of zinc is afterwards precipitated from the solution which is filtered from the sulphate of barytes.

Separation from the Fixed Alcalies.—Oxide of zinc is separated from the fixed alcalies, by rendering the solution ammoniacal, and precipitating the zinc in the state of sulphuret. The filtered solution is acidulated, heated, and again filtered. It is then evaporated to dryness, and the dry mass is ignited. The remainder consists of the fixed alcalies, combined with the acid with which they were combined before the separation; provided, however, that the acid be not one of those whose salts are decomposed by ignition.

XVI. COBALT.

Precipitation of Oxide of Cobalt by Caustic Potash.—The oxide of cobalt is best precipitated from its solutions by caustic potash. The precipitate is bulky, and of a blue colour, which, after some time, passes into green. It is proper to precipitate the oxide from a hot solution, or to boil the solution after precipitation. The colour of the precipitate thereupon changes, and after long boiling, becomes dirty rose red. This, however, is not always the case, even when the solution of cobalt has been previously diluted with an equal quantity of water. The precipitated oxide is washed clean with difficulty. The washing succeeds best with hot water. After being washed, it is dried and ignited, upon which it turns black; it is then weighed.

Reduction of Oxide of Cobalt by Hydrogen Gas.—According to the above method, however, it is not possible to determine with accuracy the quantity of the oxide of cobalt, nor is it possible even to approach exactness. After repeatedly igniting the oxide, the operator continually obtains a different weight; and the weights obtained in this manner always indicate a greater quantity of oxide of cobalt than the experiments ought to produce. The reason of this is, that the oxide, during the ignition, becomes more highly oxidised, which is a mischance which cannot be avoided, not even when the ignited oxide is quickly cooled in a closed crucible. In order to determine with accuracy the quantity of cobalt contained in the ignited oxide, it is best to convert a weighed quantity of it, by means of hydrogen gas, into reguline cobalt, and to calculate from the weight of the resulting metal that of the whole quantity of the oxide. The reduction is performed in the following manner: In the flask *a*, which contains zinc and water, the operator pours sulphuric acid through the funnel *b*, and thus produces, in the ordinary manner, the disengagement of a gentle current of hydrogen gas. This escapes through a glass tube, which is bent at a right angle, and furnished with two bulbs *c c*, in which the greater part of the moisture of the gas condenses. In order to dry it completely, it is next led through a glass tube *d*, filled with chloride of calcium. It is then allowed to pass through the glass bulb *g*, over the ignited oxide of cobalt. The bulb *g* must be of strong and difficultly fusible glass, and must have a glass tube joined to each side. It is first weighed empty, and after the oxide of cobalt has been placed in the bulb, and the tubes have been cleansed by the plume of a feather from the particles of oxide which may have soiled them, it is again weighed. By this means, the operator learns the quantity of the oxide employed in the experiment. The different parts of the apparatus are connected together by tubes of Indian rubber. When the whole apparatus is filled with hydrogen gas, a gentle heat is applied to the glass bulb *g*, which



contains the oxide of cobalt. The heat is gradually increased until, at last, the bulb is heated to full redness. This strong ignition is indispensable, because the reduced cobalt might otherwise possess the pyrophoric property of inflaming on the admission of atmospheric air. This operation produces water, part of which flies off with the excess of hydrogen gas, and part is deposited in drops in the terminating glass tube of the bulb *g*, whence it must be expelled by the flame of a small spirit lamp. When no more water is produced, all the oxide of cobalt is converted into metal. The operator then ceases to heat the bulb, but during the cooling of the reguline cobalt still continues to pass hydrogen gas through the apparatus. When the whole is completely cold, the bulb *g*, with the reduced cobalt, is weighed; the operator thus learns the quantity of metal in the weighed quantity of the oxide employed, since the difference of weight in the two last weighings indicates the quantity of oxygen which was contained in the oxide of cobalt. From the proportion of the metal and of oxygen in the quantity of oxide submitted to analysis, the quantity of *both* in the whole quantity of the oxide which could not have been reduced by such an experiment, is calculated. If the substance submitted to examination, contained the cobalt in the state of oxide, then the quantity of oxide must be calculated from the quantity of metal obtained.—When the oxide of cobalt submitted to reduction has not been well washed, and contains foreign substances, especially alumina, the reduced metal possesses the pyrophoric property of inflaming upon the admission of atmospheric air, even when it has previously been very strongly ignited.

Precipitation by Carbonate of Potash.—The oxide of cobalt is not precipitated from its solutions so completely by carbonate of potash as by caustic potash, not even when the solutions are boiled with it, and do not contain ammoniacal salts. Nevertheless, if proper precautions are taken, the oxide of cobalt can be so completely precipitated by carbonate of potash, that no traces of it can be detected in the filtered liquid by the reaction of bihydrosulphuret of ammonia.

Precipitation by Bihydrosulphuret of Ammonia.—When a solution, from which oxide of cobalt is to be precipitated, contains free ammonia or ammoniacal salts, the oxide of cobalt cannot be precipitated by caustic potash. The operator, it is true, can mix the solution with a sufficient quantity of carbonate of potash, and then gradually decompose the ammoniacal salts by evaporation. This method, however, is very indirect, and even when the evaporation is carried on to dryness, does not give an accurate result, because the oxide of cobalt is not fully precipitated by alcaline carbonates. The process is the more troublesome in proportion as the quantity of the ammoniacal salts is the more considerable. By the evaporation of the solution to dryness, the oxide is converted into peroxide. It is, consequently, better and shorter, in these cases, to precipitate the cobalt by bihydrosulphuret of ammonia, in the state of sulphuret of cobalt. The solution of cobalt must be neutral, or may be made ammoniacal, as the sulphuret of cobalt is quite insoluble in free alcalies. The sulphuret of cobalt forms a black precipitate, which is less voluminous than the sulphuret of iron, and less disposed than that substance to become oxidised in the air. The sulphuret of cobalt is edulcorated with water, mixed with bihydrosulphuret of ammonia, which is better adapted to the purpose than pure water. In order to find the quantity of cobalt contained in the sulphuret of cobalt, the latter is taken still wet from the funnel, placed with the filter in a glass, and digested warm with nitric acid or aqua regia, until all the cobalt is dissolved, and nothing remains undissolved but the yellow sulphur. Muriatic acid alone does not effect the decomposition of the sulphuret of cobalt. The solution is diluted with water, and filtered, and the insoluble remainder is washed. The oxide of cobalt is then precipitated from the solution by means of caustic potash. The oxide so obtained is ignited and weighed, and a portion of it is reduced by hydrogen gas. From the weight of the metal furnished by this portion, the quantity of cobalt contained in the whole quantity of oxide is calculated.

Separation from Oxide of Zinc.—The separation of oxide of cobalt from other substances is often accompanied by many difficulties. It cannot be separated by caustic potash from oxide of zinc, not even when the solution of both metals is boiled with a great excess of caustic potash. It is true, that the oxide of zinc is dissolved in this operation, but the oxide of cobalt which remains undissolved still contains a great quantity of oxide of zinc, and this is incapable of being separated by any excess of caustic potash. The only method of completely separating these two oxides, consists in converting them into chlorides, and in separating the volatile chloride of zinc from chloride of cobalt, by distillation, while a current of muriatic acid gas is passed through the apparatus. The operator begins by precipitating both substances in the state of carbonates, by means of carbonate of potash. If the solution contains ammoniacal salts, the precipitation must be effected by means of an excess of carbonate of potash, and with the precautions which are necessary to be observed in the precipitation of oxide of zinc alone (page 74). The filtered solution can still retain a little oxide of cobalt, which must be precipitated by bihydrosulphuret of ammonia, and examined apart.—The carbonates are ignited, and thus deprived of their carbonic acid. The resulting oxides are then weighed, and treated in an apparatus similar to that depicted at page 77. The process is precisely similar to that recommended for separating the oxides of zinc and manganese.

Separation from Peroxide of Iron.—Oxide of cobalt can be separated from peroxide of iron by the process employed to separate peroxide of iron from protoxide of manganese. The solution of both substances, especially when only a small quantity of peroxide of iron is present, is mixed with a solution of sal ammoniac, which possesses the property, when added in sufficient quantity, of hindering the precipitation of oxide of cobalt by caustic ammonia. If the solution is very acid, the addition of sal ammoniac is unnecessary. The solution is then saturated with ammonia, the precautions being observed which have been pointed out at page 55. The peroxide of iron is thereupon precipitated by a neutral alcaline succinate, and the succinate of iron is treated in the manner which has been formerly described. The solution, filtered from the succinate of iron, contains the oxide of cobalt; it is precipitated by bihydrosulphuret of ammonia, in the state of sulphuret of cobalt, which is treated in the manner already particularised. —Peroxide of iron and oxide of cobalt can also be separated by ammonia; but in this case, it is necessary to add a very large quantity of sal ammoniac to the solution. If, however, the solution is very acid, this addition of sal ammoniac is unnecessary. This method of precipitating the peroxide of iron by ammonia, instead of by succinate of ammonia, and of thereby separating it from oxide of cobalt, is particularly to be recommended, when the quantity of peroxide of iron is very small in comparison with that of the oxide of cobalt.—When protoxide of iron is to be separated from oxide of cobalt, it is necessary to convert the protoxide of iron into the peroxide, previous to attempting the separation.

Separation from Protoxide of Manganese.—The separation of oxide of cobalt from protoxide of manganese is accompanied by many difficulties. It can only be accomplished by converting both oxides into chlorides, and treating these with hydrogen gas. Hereupon, the chloride of cobalt is reduced to metallic cobalt, while the chloride of manganese remains unaltered. The operator begins by precipitating the two oxides together. This can be effected by caustic potash, provided that the solution contains neither free ammonia nor ammoniacal salts. But if these are present, it is necessary to employ carbonate of potash in excess, and to evaporate the solution to dryness. The operator can also, which is better, precipitate both oxides from a neutral or ammoniacal solution by bihydrosulphuret of ammonia. He must then decompose the sulphurets by nitric acid, and precipitate the oxides of both metals from the nitric acid solution by caustic potash. The oxides are washed, ignited, and weighed. Such a quantity as may be thought necessary is then placed in a glass bulb, which has a glass tube joined to each side; the bulb is heated, and a current of muriatic acid gas is meanwhile passed over the substance, to convert the oxides into chlorides. For the disengagement of the muriatic acid gas, a flask, similar to that depicted in the apparatus described at page 77, is employed. The operation continues very long before the oxides are completely converted into chlorides; and it would, therefore, be far more advantageous to convert the oxides into chlorides, by solution in muriatic acid. But when the chlorides are prepared in this manner, it is impossible to bring a determinate quantity into a glass bulb with accuracy. The chlorides being prepared, dry hydrogen gas is passed through the apparatus, while the bulb in which the chlorides are placed is strongly heated. The same apparatus is employed for this purpose as for the reduction of oxide of cobalt. It is depicted at page 83. The disengagement of hydrogen gas is not interrupted, until the quantity of muriatic acid gas which issues from the apparatus is very inconsiderable. The operation can never be brought to such a nicety, as to cause a discontinuance in the production of muriatic acid gas; for even when the chloride of cobalt is completely reduced, there is still a disengagement of exceedingly slight traces of muriatic acid gas from the chloride of manganese. The latter, it is true, is not decomposed by the hydrogen gas, and yet, when exposed to a strong heat, it attacks the glass. So soon, therefore, as only inconsiderable white clouds appear, when a glass rod moistened with ammonia is held at the end of the apparatus where the excess of gas escapes, the glass bulb is allowed to cool, the disengagement of hydrogen gas being, however, continued during the cooling. When the whole is cold, the glass bulb is placed in water, upon which the chloride of manganese is dissolved, while the metallic cobalt, in a state of fine division, remains insoluble. The chloride of manganese is, however, not completely dissolved: brown flocks of it appear in the liquid, and increase in quantity when it is long exposed to the atmosphere. But these flocks dissolve upon the addition of a few drops of muriatic acid. As they remain suspended in the liquid longer than the metallic cobalt, they can be poured from the latter with the solution of chloride of manganese. The operator now treats the cobalt with water, made weakly acid by the addition of a few drops of diluted muriatic acid. This liquid dissolves completely the remaining traces of manganese, while it does not attack the cobalt. It is proper to decant it very soon, however, and to wash the cobalt again with pure water. It can be filtered on a weighed filter, quickly dried by exposure to a moderate heat, and then weighed. If the operator desires to reach the utmost degree of accuracy, he may redissolve the cobalt in nitric acid, and precipitate the solution by caustic potash; he will then have to treat the oxide of cobalt in the manner which has already been described.—From the solution of chloride of manganese, separated in the above process, the protoxide of manganese is precipitated by carbonate of potash, according to the instructions which have been given at page 42.

Separation from Alumina.—The oxide of cobalt is separated from alumina by caustic potash. The oxide of cobalt is precipitated, while the alumina remains in solution.

Separation from Magnesia.—From magnesia, the oxide of cobalt is best separated by the process which follows: The operator adds to the solution of both, so much sal ammoniac, that upon the addition of ammonia, neither magnesia nor oxide of cobalt precipitates. If the solution is acid, the addition of sal ammoniac is unnecessary. He then adds bihydrosulphuret of ammonia; the sulphuret of cobalt hereby precipitated is filtered and washed with water, to which a little bihydrosulphuret of ammonia has been added. In order to determine the quantity of cobalt contained in the sulphuret, it is treated in the manner which has been described above.—Previous to effecting the quantitative determination of the magnesia, the excess of bihydrosulphuret of ammonia existing in the solution filtered from the sulphuret of cobalt, must be destroyed by an acid.

Separation from Lime.—The oxide of cobalt is separated from lime by oxalate of ammonia. The solution of both substances is mixed with so much sal ammoniac, that upon the addition of an excess of caustic ammonia no oxide of cobalt precipitates. When the solution is acid, the addition of sal ammoniac is unnecessary. The lime is then precipitated by oxalate of ammonia, and the oxide of cobalt is precipitated from the solution filtered from the oxalate of lime, according to the process which has been described above. But it is, in this case, necessary to filter the oxalate of lime very quickly, and to protect the solution, during the operation, as much as possible from the contact of atmospheric air, in order that the oxide of cobalt contained in the ammoniacal liquid may not become more highly oxidised. As the oxalate of cobalt can only be held in solution by a great quantity of ammonia, this method of separating lime and oxide of cobalt, though generally followed, is not to be recommended. A better result is obtained in the following manner: The ammoniacal solution of both substances is mixed with bihydrosulphuret of ammonia, by which means the cobalt is precipitated in the state of sulphuret of cobalt. This precipitate must be quickly filtered, care being taken to hinder the access of atmospheric air during the filtering. The object of this is to prevent the formation of carbonate of lime, and the consequent contamination of the sulphuret of cobalt. The solution, filtered from the sulphuret of cobalt, is first treated with muriatic acid, for the purpose of decomposing the excess of bihydrosulphuret of ammonia; the operator can then precipitate the lime. In performing this process, it is proper to allow the sulphuret of cobalt full time to subside in a flask which can be corked; the solution containing the lime then runs quickly through the filter, before any portion of carbonate of lime has time to form, in consequence of the access of atmospheric air.

Separation from Strontian.—The oxide of cobalt is separated from strontian by the same process that is employed to separate it from lime. The separation could also be effected by sulphuric acid.

Separation from Barytes.—From barytes, the oxide of cobalt can be separated by sulphuric acid. From the solution, filtered from the sulphate of barytes, the oxide of cobalt is precipitated by caustic potash.

Separation from the Fixed Alcalies.—The oxide of cobalt is separated from the fixed alcalies, by adding to the neutral or ammoniacal solution, bihydrosulphuret of ammonia, which precipitates sulphuret of cobalt. In the solution, which is filtered from this precipitate, an acid is poured to decompose the excess of bihydrosulphuret of ammonia. The quantity of the alcalies is then determined in the manner which has been already explained.

XVII. NICKEL.

Precipitation as Oxide of Nickel, by Caustic Potash.—The oxide of nickel, like the oxide of cobalt, is best precipitated from its solutions by caustic potash. It forms an apple green voluminous precipitate, and the precipitation is so complete, that, when the operation has been performed with proper care, and particularly when the whole has been boiled, it is impossible to detect, by reagents, the least trace of oxide of nickel in the filtered solution. The precipitate can be washed clean with difficulty; on which account, hot water must be used for the purpose. After being washed, it is dried, ignited, and weighed. The ignition renders it black. It then consists of pure oxide, which, on being repeatedly heated and cooled, suffers no change of weight. It is, therefore, unnecessary to reduce the ignited oxide of nickel by hydrogen gas. The estimation of oxide of nickel is, consequently, simpler than the estimation of oxide of cobalt.—The precipitation of oxide of nickel must always be effected by caustic potash, since its precipitation by carbonate of potash is by far less complete.—Caustic potash completely precipitates oxide of nickel, not only from solutions which contain muriate of ammonia or other ammoniacal salts, and that even in the cold, but also from solutions which contain free ammonia. By this behaviour towards caustic potash, oxide of nickel is strikingly distinguished from oxide of cobalt.

Precipitation as Sulphuret of Nickel.—Precipitation from neutral or ammoniacal solutions, by bihydrosulphuret of ammonia, does not succeed so well with oxide of nickel as with oxide of cobalt. The reason of this is, that sulphuret of nickel is somewhat soluble in bihydrosulphuret of ammonia, with which it forms a brown solution. This solution, in a concentrated state, is perfectly opaque. Upon being evaporated, it again deposits, according to **Berzelius** (**Schweigger's** Jahrbuch, T. xxxii. p. 166), a portion of sulphuret of nickel; another portion, however, becomes oxidised, and remains in solution.—The precipitation of nickel, as sulphuret of nickel, from a neutral or ammoniacal solution, succeeds best when the operation is performed as follows: The solution is diluted with a large quantity of water, and mixed with bihydrosulphuret of ammonia, of which a very great excess is to be avoided. The glass is then covered with bibulous paper, and placed for some time where it is exposed to a very gentle heat. The excess of bihydrosulphuret of ammonia is slowly destroyed by the oxygen and carbonic acid of the atmosphere, while the precipitated sulphuret of nickel remains unoxidised. When the supernatant fluid has no longer a brownish colour, it is filtered, and the sulphuret of nickel is quickly washed with water, to which a very small quantity of bihydrosulphuret of ammonia has been added. When proper precaution is taken, the process is so completely successful, that the solution filtered from the sulphuret of nickel is found to be wholly free from nickel. The sulphuret of nickel is then digested with the filter, in nitric acid or aqua regia, until the sulphur which is separated assumes a yellow colour. The solution is filtered; the sulphur, forming the insoluble remainder, is washed; and the oxide of nickel, in the solution, is precipitated by caustic potash. The weight of the oxide of nickel must now be determined. Instead of nitric acid or aqua regia, one must not employ muriatic acid in this operation, because the latter is incapable of fully decomposing the sulphuret of nickel.—It is impossible, or nearly impossible, to succeed in completely destroying the excess of bihydrosulphuret of ammonia existing in a solution of oxide of nickel, by the addition of a weak acid, without, at the same time, decomposing a portion of the precipitated sulphuret of nickel. If the smallest quantity of acid be added in excess, the liquid filtered from the sulphuret of nickel is sure to hold a portion of nickel in solution.

Separation from Oxide of Cobalt.—The separation of nickel and cobalt is attended by difficulties; and the most celebrated chemists have recommended methods of separation more or less adequate to the purpose. The question here is not, how can one obtain oxide of nickel free from oxide of cobalt, without paying attention to the quantity of the oxide of nickel? The question is,—in what manner can the quantitative separation of both oxides be effected? The best method is that of PHILLIPS, which is employed by BERZELIUS (SCHWEIGGER'S Jahrbuch, T. XXXII. p. 171). Both oxides are dissolved in an acid, and the solution is supersaturated with ammonia. If a portion of oxide of cobalt precipitate, there is not a sufficient quantity of ammoniacal salt in the solution. More acid must be added, and then must be again supersaturated with ammonia. Or, a sufficient quantity of muriate of ammonia may be added at once, and the solution be then supersaturated with ammonia, upon which no precipitate will be formed. The solution now assumes a sky blue colour, even when the quantity of oxide of cobalt is greater than that of oxide of nickel. It is diluted with much water. The greater the quantity of oxide of cobalt in the solution, the more water must be added to it. The water must previously be boiled for some time, to free it from atmospheric air. The diluted solution, while still hot, is poured into a glass which can be corked. Caustic potash is then added, and the vessel is closed. Oxide of nickel alone is precipitated from the ammoniacal solution by the caustic potash; the oxide of cobalt remains in solution. If, after the addition of the caustic potash, and the subsiding of the precipitate, the solution has completely lost its blue colour, and appears bright or deep red, in consequence of holding oxide of cobalt in solution, it may be presumed that the caustic potash has been added in sufficient quantity. When the oxide of nickel has fully deposited itself, the supernatant liquid is poured through a filter, and the oxide of nickel is afterwards brought upon the filter, and washed with hot water. The reason why it is necessary to dilute the solution of the two oxides with water freed from air, is, that oxide of cobalt in an ammoniacal solution, is very easily converted into peroxide of cobalt, which, precipitating as a black powder, would contaminate the oxide of nickel. The more dilute the solution is, the less easily does the oxide of cobalt become more highly oxidised. The quantity of caustic potash required in this case to precipitate the oxide of nickel, is very considerable, when the solution contains a very large quantity of ammonia. On this account, when no precipitate appears on the first addition of caustic potash to the ammoniacal solution, the operator must add fresh quantities of the precipitant, and not too readily take up the opinion that no oxide of nickel is present.—The best method of separating the oxide of cobalt from the solution filtered from the oxide of nickel, is to precipitate it by bihydrosulphuret of ammonia, and to treat the sulphuret of cobalt in the manner which has been described at page 85.

Separation from Oxide of Zinc.—The separation of oxide of nickel from oxide of zinc can be effected only by the process employed to separate oxide of cobalt from oxide of zinc. It is, therefore, much easier to separate oxide of nickel from oxide of cobalt, than to separate it from oxide of zinc. If, with a view to separate the two oxides, a solution of caustic potash be added to dissolve the oxide of zinc, the separation cannot then be completely effected; because the greatest excess of caustic potash is incapable of dissolving the whole of the oxide of zinc, even when the mixture is boiled. It is, indeed, true, that oxide of zinc dissolves in caustic potash, but in this case, a very considerable proportion falls down with the oxide of nickel. The same thing takes place when both oxides have been dissolved in ammonia: upon the addition of a solution of caustic potash, oxide of zinc is dissolved, but the precipitated oxide of nickel is very zinciferous.—The analyst is obliged, therefore, to convert the oxides into chlorides, and to separate the chloride of zinc from the chloride of nickel by volatilization. The method of proceeding is precisely the same as in the separation of chloride of zinc from chloride of manganese, or chloride of cobalt. The manipulation has been described at pages 76 and 86.—If the compound to be examined contains nickel and zinc in the metallic state, as, for example, is the case with several metallic alloys which have of late been employed as substitutes for silver, then the zinc cannot be separated from nickel and other metals, by exposing the alloy to the direct action of heat and dry chlorine gas. The conversion of the metals into chlorides is, indeed, very easily effected, and the combination of the metals with the chlorine is attended by incandescence. It is impossible, however, to separate accurately, by volatilization, the water-free chloride of zinc from the chlorides which accompany it. It appears, that the chloride of zinc must contain water, to render it easily separable, by distillation, from other chlorides.—A metallic compound of zinc and nickel must, consequently, be analysed in a different manner. The operator dissolves it in nitric acid, and precipitates the oxides from the boiling solution by carbonate of potash. He converts the precipitated carbonates into chlorides, and distils the chloride of zinc from the chloride of nickel. —If other metals are contained in the compound, they must be separated in a different manner. Should copper be present, it must be separated by a process which will be described farther on, under the article Copper.—The operator must continually bear in mind, when engaged in these processes, that oxide of nickel is not completely precipitated by carbonate of potash.

Separation from the Oxides of Iron.—Peroxide of iron can be separated from oxide of nickel, in the same manner as from oxide of cobalt. To the solution of both substances, a sufficient quantity of muriate of ammonia, or of other ammoniacal salts, is added, and the peroxide of iron is precipitated by ammonia. The precipitate is quickly filtered and washed. The oxide of nickel is precipitated from the filtered solution by caustic potash. By following this process, a better result is obtained than by precipitating the peroxide of iron by an alcaline succinate. When the solution is extremely acid, the addition of muriate of ammonia is, of course, unnecessary.—If protoxide of iron is to be separated from oxide of nickel, the process commences with the conversion of the protoxide of iron into peroxide. The operator then proceeds as is described above.

Separation from Manganese.—The separation of the protoxide of manganese from the oxide of nickel is very difficult. It can be effected, however, in the same way as the separation of the protoxide of manganese from the oxide of cobalt. The process has been described at page 87.

Separation from Alumina.—Alumina is separated by caustic potash, much in the same way from oxide of nickel as from oxide of cobalt.

Separation from Magnesia.—As the complete precipitation of oxide of nickel, in the state of sulphuret of nickel, by bihydrosulphuret of ammonia, is produced with much difficulty, the separation of oxide of nickel from magnesia cannot be effected without a great deal of trouble. The best method of proceeding is the following: To the solution of both substances, so much muriate of ammonia is added, that no precipitate is produced on the subsequent addition of ammonia. The oxide of nickel is then precipitated by bihydrosulphuret of ammonia, as sulphuret of nickel. When the solution of the two oxides is acid, the addition of muriate of ammonia is unnecessary. A great excess of bihydrosulphuret of ammonia is avoided as much as possible. The whole is placed in a gently-warmed situation, being at the same time exposed to atmospheric air, until the sulphuret of nickel has completely subsided. The solution is then filtered, and the sulphuret of nickel is washed with water, to which a very small portion of bihydrosulphuret of ammonia has been added. The sulphuret of nickel is afterwards to be treated in the manner which has been described above. The filtered solution is acidulated by an acid, then warmed, and again filtered. The operator then precipitates the magnesia.—It is impossible to separate magnesia from oxide of nickel, by adding to an ammoniacal solution, a solution of phosphate of soda, with a view to precipitate the magnesia. This produces, indeed, a precipitate of phosphate of ammonia and magnesia; but the precipitate contains oxide of nickel, which gives it a greenish colour, and no excess of ammonia is sufficient to effect the complete separation of the oxide of nickel from the precipitated salt of magnesia.

Separation from Lime.—Oxide of nickel is separated from lime as follows: The diluted solution of both substances is rendered ammoniacal, and the lime is precipitated by oxalate of ammonia. The oxalate of lime is quickly filtered, and the oxide of nickel is precipitated from the filtered solution by caustic potash.

Separation from Strontian and Barytes.—From strontian and barytes, oxide of nickel is separated by sulphuric acid, by which the two former are precipitated. The oxide of nickel is precipitated from the filtered solution by caustic potash.

Separation from Fixed Alcalies.—Oxide of nickel is separated from the fixed alcalies in the same manner as from magnesia; that is to say, it is precipitated, with proper precaution, by bihydrosulphuret of ammonia, in the state of sulphuret of nickel.

XVIII. CADMIUM.

Precipitation by Carbonate of Potash.—Oxide of cadmium is best precipitated from its solutions by carbonate of potash. The precipitate, which has a white colour, is dried and ignited. During the ignition, carbonic acid and water are expelled, and oxide of cadmium remains behind, in the state of a brown powder. As this oxide can be reduced by charcoal, and is then easily volatilized, it is necessary to separate the precipitate as completely as possible from the filter, and to burn the filter to ashes by itself.—Carbonate of ammonia precipitates oxide of cadmium less completely than carbonate of potash.

Separation from all the Metallic Oxides hitherto treated of.—Oxide of cadmium may be separated from all the oxides which have been hitherto treated of, by the process which follows: The solution is acidulated with an acid, for example, with muriatic acid, and is diluted with a large quantity of water. It is then exposed to the action of a slow current of sulphuretted hydrogen gas, which is allowed to pass into it continually, until the solution is so fully saturated, that it has a strong smell of sulphuretted hydrogen, even when the gas no longer passes through it. The precipitate formed in this process is sulphuret of cadmium, which is insoluble in a diluted acid solution. The oxides of nickel, cobalt, zinc, iron, and manganese are not precipitated by sulphuretted hydrogen gas from acid solutions, not even when the solutions are diluted. When it is oxide of zinc which is to be separated, by this process, from oxide of cadmium, more acid must be added to the solution than is necessary when the oxides of nickel, cobalt, iron, and manganese are to be separated.—The solutions of the earths and alcalies being incapable of precipitation by sulphuretted hydrogen gas, those substances can be thereby easily separated from oxide of cadmium.

The sulphuret of cadmium produced in these operations has a different colour, according as the solution from which it has been precipitated was more or less diluted. It is sometimes orange, sometimes yellow. It can be filtered on a weighed filter, and washed with pure water. It must afterwards be carefully dried, by the application of an extremely gentle degree of heat, until, after repeated weighings, it loses no more in weight. From the weight of the sulphuret, the quantity of the oxide or metal, according as the one or the other was contained in the substance examined, is learnt by calculation.—The operator should always convince himself, in a process of this nature, that the precipitated sulphuret of cadmium contains no admixture of free sulphur, as that would increase the apparent weight of the sulphuret of cadmium, and render the analysis inexact. The deposition of sulphur can take place, when, subsequent to precipitation by sulphuretted hydrogen gas, the solution remains very long in contact with atmospheric air; under such circumstances, the sulphuretted hydrogen, dissolved in the water, deposits sulphur. But the admixture of sulphur is also produced, when the acid solution, from which sulphuret of cadmium is to be precipitated, contains peroxide of iron. By the action of sulphuretted hydrogen gas, the peroxide of iron is reduced to protoxide; the latter remains in solution, but a quantity of sulphur is separated, and necessarily falls down with the sulphuret of cadmium. It is consequently always more advisable to redissolve the precipitated sulphuret of cadmium, and to precipitate the oxide of cadmium by a solution of carbonate of potash. The sulphuret of cadmium is taken with the filter, still wet from the funnel. It is placed in a glass with concentrated muriatic acid, and is left to digest, with the assistance of a gentle heat, until the smell of sulphuretted hydrogen is no longer perceptible. The solution is then filtered, and the oxide of cadmium is precipitated.

When oxide of cadmium has been separated in this manner from other substances, the solution filtered from the sulphuret of cadmium must be exposed to a very moderate heat, until it ceases to smell of sulphuretted hydrogen. The other substances are then to be precipitated. If peroxide of iron was present in the solution, it will have been converted, as has been explained above, into protoxide of iron. It is necessary to reconvert the protoxide of iron, by means of nitric acid, into peroxide.

Precipitation by Bihydrosulphuret of Ammonia.—Oxide of cadmium can also be completely precipitated from neutral or ammoniacal solutions, by bihydrosulphuret of ammonia. It is then necessary, however, to treat the precipitate with muriatic acid, and to reprecipitate the oxide of cadmium by carbonate of potash.

XIX. LEAD.

Precipitation by Oxalate of Ammonia.—Protoxide of lead is best precipitated from its solutions by oxalate of ammonia. In this case, as in the precipitation of lime, the solution must be either neutral or weakly ammoniacal. The oxalate of lead is washed, and dried; it is afterwards ignited in a small, open, counterpoised crucible of porcelain. By the ignition, the oxalate is converted into the protoxide. This is weighed. If the compound examined contained lead in the metallic state, the quantity is estimated from the weight of the protoxide.—If the filter, upon which the oxalate of lead has been filtered, be burnt with the precipitate, as it generally is with other precipitates, the charcoal of the paper may reduce part of the protoxide of lead to the metallic state. The oxalate of lead must therefore be removed from the filter with as

163582

much accuracy as possible, and the filter must be burnt by itself. Previous to the weighing, the ashes of the filter must be added to the ignited precipitate. The burning of the filter is best effected in the porcelain crucible, before the oxalate of lead is placed in it for ignition.—The same precaution is to be observed with all other precipitates of lead, which require to be heated to redness, with the single exception of the sulphate of lead. The ignition must, if possible, be always performed over the spirit lamp with circular wick, in small and very thin crucibles of porcelain.

Precipitation by Carbonate of Ammonia.—Protoxide of lead can also be precipitated by carbonate of ammonia, but the solution then requires to be heated. If the carbonate of ammonia, which is to be employed as the precipitant, contain much bicarbonate of ammonia, it is good to add a little caustic ammonia, otherwise the protoxide of lead will not be completely precipitated; yet, the traces of lead, which would even then remain in solution, would be extraordinarily slight. The precipitated carbonate of lead is, like the oxalate of lead, submitted to ignition in a porcelain crucible. It is thus deprived of its carbonic acid, and converted into protoxide of lead, which is then weighed.

Estimation as Sulphate of Lead.—When protoxide of lead is to be estimated in the state of sulphate, the solution must be mixed with sulphuric acid and evaporated to dryness, and the remainder must be heated in a crucible to expel the excess of sulphuric acid. The sulphate of lead is then to be weighed. During the ignition, the access of the air must be prevented, especially when the ignition occupies much time; if this is neglected, a very small portion of sulphate of lead may easily be volatilized. The ignition may be performed in a platinum crucible.

Separation from the Oxides of Nickel, Cobalt, Zinc, Iron, and Manganese, and from the Earths and Fixed Alcalies.—As protoxide of lead can be precipitated from acid solutions, by a current of sulphuretted hydrogen gas, this is the best method of separating it from all the substances hitherto treated of, excepting from cadmium; because the acid solutions of none of these substances afford a precipitate with this reagent. The best mode of procedure is to begin with acidulating the solution of the oxides, if it be neutral, by the addition of nitric acid. This must not be done with muriatic acid, since this would produce a precipitate, if the solution of lead were not exceedingly dilute. The acid solution is diluted with water, and is subjected to the action of a slow stream of sulphuretted hydrogen gas, until the liquid is completely saturated with the gas. In the beginning of the process, when only a few bubbles of the gas have passed through the solution, the precipitate often appears to have a reddish brown colour; but when a more considerable quantity of sulphuretted hydrogen gas has passed through the solution, the precipitate becomes perfectly black. This is particularly the case when the solution contains muriatic acid, or when sulphuretted hydrogen gas is employed to precipitate a solution of chloride of lead.—The precipitated sulphuret of lead could be filtered on a weighed filter, washed with pure water, and carefully dried by a very gentle heat, until, after repeated weighings, it was found to lose no more in weight. The quantity of protoxide of lead, could then be determined from the weight of the sulphuret of lead. When, however, free sulphur has precipitated with the sulphuret of lead, which, for example, is always the case when the solution contains peroxide of iron, it is good to convert the sulphuret of lead into sulphate of lead. To this end, the precipitate is pretty well dried, and is placed, with the filter, which must be as small as possible, in a glass or a large platinum capsule. It is then subjected to the action of concentrated fuming nitric acid. This must be added in very small quantities, and with very great precaution. The too sudden, or too rapid addition of the acid, would cause so violent an action, that a portion of the mass might be thrown out of the vessel, and lost. The glass or the platinum capsule must be carefully covered with a glass plate. The sulphuret of lead is hereby completely converted into sulphate of lead. If the operator uses nitric acid which does not fume, a separation of sulphur takes place, and this sulphur does not become fully oxidised even after a long digestion. When the action of the nitric acid on the sulphuret of lead is at an end, the resulting sulphate of lead must be exposed to a moderate heat, until it no longer exhales any acid vapours. It is then ignited. The organic matter furnished by the filter is thus destroyed, and, in consequence of the presence of atmospheric air, burns away without causing the reduction of any sulphate of lead. After ignition, the sulphate of lead is weighed.—The sulphuret of lead can also be treated with concentrated muriatic acid, which disengages sulphuretted hydrogen gas. Nitric acid is then added, and the whole is evaporated to dryness. The filter is thereby completely oxidised. The dry mass is transferred to a porcelain crucible, mixed with sulphuric acid, and heated until the excess of sulphuric acid is driven away. The resulting sulphate of lead is then weighed. It is not advisable to estimate the chloride of lead, obtained from the sulphuret, as chloride. It should always be converted into sulphate.—The solution, filtered from the sulphuret of lead, is first warmed, until it no longer smells of sulphuretted hydrogen. The operator then proceeds to estimate the remaining substances. If peroxide of iron was combined with the protoxide of lead, it will have been reduced, by the action of the sulphuretted hydrogen gas, to protoxide of iron. The solution must therefore be treated with nitric acid, to reconvert the protoxide into peroxide. This method of separating protoxide of lead from substances, which sulphuretted hydrogen gas is incapable of precipitating from acid solutions, is preferable to every other method of separation. It is a better method, for example, than that in which the protoxide of lead is precipitated, by sulphuric acid, from oxides, with which sulphuric acid forms salts which are soluble.—The oxides, from which protoxide of lead can be separated by sulphuretted hydrogen gas, are the oxides of nickel, cobalt, zinc, iron, and manganese, and the earths and alcalies.

Precipitation by Bihydrosulphuret of Ammonia.—Protoxide of lead can be completely precipitated from neutral or ammoniacal solutions by bihydrosulphuret of ammonia.

The resulting sulphuret of lead must, however, be converted into sulphate of lead.

Separation from Oxide of Cadmium.—Protoxide of lead and oxide of cadmium, are best separated by mixing the solution of both oxides with sulphuric acid, evaporating the solution to dryness, and heating the remainder until the excess of sulphuric acid has been expelled. The dry mass is then treated with water: the sulphate of cadmium dissolves, and the sulphate of lead remains behind. The solution is filtered, and the sulphate of lead is washed with water, of which, however, but little dare be used, since sulphate of lead is not altogether insoluble therein. The sulphate of lead is then dried, and ignited. The filter is burnt first, on the cover of the platinum crucible. From the filtered solution, the sulphate of cadmium is precipitated by carbonate of potash.—The result afforded by this method is not extraordinarily accurate, as the sulphate of lead is not quite insoluble in water. No other method of separation has, however, been yet discovered.

XX. BISMUTH.

Precipitation by Carbonate of Ammonia.—The best precipitant of oxide of bismuth is carbonate of ammonia, which, when added to the solution in excess, precipitates the oxide of bismuth completely. It is quite immaterial whether the bismuth be contained in a clear, diluted, acid solution, or in a solution which has been rendered milky by dilution with water. At first, the carbonate of ammonia dissolves a large quantity of the oxide of bismuth; but, when the whole has remained in a warm place for some hours, the whole of the oxide of bismuth precipitates, or, at any rate, the quantity which remains in solution is imponderable. The precipitate is easily washed clean. After being dried, it is ignited in a porcelain crucible. It loses its white colour thereby, and becomes yellow. Unless the heat of the spirit lamp be too strong, it does not melt. The filter is separated as accurately as possible from the precipitate, and burnt to ashes by itself.—Carbonate of potash precipitates oxide of bismuth as completely as carbonate of ammonia does. The precipitate, however, always contains traces of potash, which are not easily separable by washing. Carbonate of soda precipitates oxide of bismuth less perfectly.

Separation from Chlorine.—When oxide of bismuth is to be quantitatively estimated by carbonate of ammonia, the solution must be entirely free from muriatic acid. If this be not the case, the oxide is still completely precipitated; but the precipitate is contaminated by chloride of bismuth, which no excess of the precipitant, nor even of carbonate of potash, can completely decompose. When such a precipitate is dried and ignited, chloride of bismuth sublimes, while oxide of bismuth remains behind, still mixed with a portion of chloride. In analyses, therefore, bismuth or oxide of bismuth dare be dissolved in nitric acid alone, and never in aqua regia. Should oxide of bismuth fall to be estimated in a solution containing muriatic acid, it must be separated as sulphuret of bismuth. The muriatic acid solution is mingled with caustic ammonia, and bihydrosulphuret of ammonia; thereupon, sulphuret of bismuth precipitates. The precipitate, after being washed, is taken with the filter still moist from the funnel, and submitted to the action of nitric acid. The sulphuret of bismuth is thus decomposed, even in the cold. It is, however, digested in a moderate heat, until the separated sulphur is completely yellow. The solution is filtered, and the sulphur is washed with water which has been acidulated by nitric acid. The oxide of bismuth is then precipitated by carbonate of ammonia.

Separation from Protoxide of Lead.—To separate oxide of bismuth from protoxide of lead, the solution of both substances is mixed with an excess of sulphuric acid; it is then evaporated, until the excess of sulphuric acid begins to volatilize. Water is then added to the mixture. Thereupon, the sulphate of bismuth completely dissolves, forming, if a sufficient excess of sulphuric acid be present, a clear solution. On the contrary, the sulphate of lead remains undissolved: the solution is filtered, and the sulphate of lead is washed with water containing a little sulphuric acid. It is then dried, and ignited. The oxide of bismuth, in the filtered solution, is precipitated by carbonate of ammonia.—The result afforded by this method of separating bismuth and lead, is not particularly accurate, since the sulphate of lead is not entirely insoluble, either in water or acid solutions. Sulphuric acid, however, dissolves less of it than any other acid does.—Since oxide of bismuth is perfectly precipitated by carbonate of ammonia, when the solution is mixed with an excess of that reagent and allowed to repose for some time, it is clear that carbonate of ammonia can effect no accurate separation of bismuth from lead. Yet this is a process which has been recommended (*Annales de Chimie,* T. XXXVI. p. 332). The analyst is directed to dissolve the oxide of bismuth in an excess of carbonate of ammonia, and to filter it from the undissolved carbonate of lead.

Separation from Oxide of Cadmium.—No method of separating oxide of bismuth from oxide of cadmium has yet been made known.

Separation from the Oxides of Nickel, Cobalt, Zinc, Iron, and Manganese, and from the Earths and Alcalies.—Oxide of bismuth is separated by sulphuretted hydrogen gas from all other oxides whose acid solutions give no precipitate with that reagent. The acid solution of oxide of bismuth must, however, be diluted, when sulphuret of bismuth is to be precipitated by sulphuretted hydrogen gas. But as solutions of oxide of bismuth become milky on being diluted with water, it is necessary to commence by adding acetic acid to the solution. The subsequent addition of water then occasions no troubling of the liquid. When the solution has been diluted, the sulphuretted hydrogen gas is led through it. The precipitated sulphuret of bismuth is decomposed by nitric acid, in the manner which has been described above. The oxide of bismuth is then precipitated from the nitric acid solution, by carbonate of ammonia.—Oxide of bismuth is separated in the above manner from the oxides of nickel, cobalt, zinc, iron, and manganese, and from the earths and alcalies. The substances which were combined with the oxide of bismuth, are contained in the solution filtered from the sulphuret of bismuth. They are now to be precipitated.—When, however, these substances are not precipitable by carbonate of ammonia, as, for example, is the case with the fixed alcalies, then the oxide of bismuth may be separated from them by the simple addition of carbonate of ammonia. The precipitation by sulphuretted hydrogen gas is thus avoided.

XXI. URANIUM.

Precipitation by Caustic Ammonia.—Peroxide of uranium is completely precipitated from its solutions by caustic ammonia. The precipitate is yell , and, in addition to peroxide of uranium, contains ammonia and water. It must not be washed with pure water, otherwise it gradually passes through the filter, and forms a yellowish milky solution. This can only be avoided by edulcorating the precipitate with a dilute solution of muriate of ammonia; yet, even then the passing of the precipitate through the filter is not totally hindered. After being washed, the precipitate is dried, and ignited. The ignition causes the expulsion of water, ammonia, and oxygen, and the peroxide of uranium is converted into protoxide. The protoxide is weighed, and the quantity of peroxide is calculated.—If the solution contain protoxide of uranium, this also is precipitated by caustic ammonia. It falls down in brown, or somewhat purple-coloured flocks, which are hydrate of protoxide of uranium. During the drying, a portion of the hydrate, according to Arfvedson, (Poggendorff's Annalen, B. I. p. 255), becomes oxidised, and acquires a yellow colour. If it has been precipitated by a great excess of ammonia, or if it has been washed with warm water, the whole precipitate is converted by the drying into ammoniacal peroxide of uranium. Upon being ignited, however, it is reconverted into protoxide.

If a solution, from which peroxide of uranium is to be precipitated, contain a considerable quantity of any earth, the precipitate, thrown down by ammonia, not only contains the peroxide of uranium, but, according to the experiments of Arfvedson, much of the earth which provided a sufficient quantity of alcohol has been added. After the evaporation of the alcohol, the peroxide of uranium is precipitated by ammonia.—From barytes, the peroxide of uranium is separated by sulphuric acid, which throws down sulphate of barytes.—To separate peroxide of uranium from the fixed alcalies, an excess of caustic ammonia is added to the solution. The resulting precipitate is washed with a solution of muriate of ammonia. The fixed alcalies are separated from the filtered solution.

XXII. COPPER.

Precipitation by Caustic Potash.—The best reagent for precipitating the deutoxide of copper is caustic potash. The solution containing the deutoxide of copper is heated in a porcelain capsule, or, what is better, in a platinum capsule; it is carefully brought to the boiling point, and while boiling, is mixed with a solution of caustic potash: thereupon the deutoxide of copper forms a heavy brownish black precipitate. If the precipitation of the deutoxide of copper be effected in the cold, it produces the hydrate of deutoxide of copper, which forms a bulky blue precipitate. This hydrate, however, when boiled, becomes denser, and of a brownish black colour, and is converted into deutoxide of copper. The deutoxide of copper is washed clean with difficulty; the washing succeeds best with hot water, because this is capable of completely dissolving the last traces of potash. When the precipitate is dry, it must be ignited. The ignition can be very well performed in a platinum crucible. The filter is burnt with the precipitate. If any of the deutoxide of copper should thereby be reduced to protoxide, the latter easily reoxides itself in the current of air produced during the ignition. The deutoxide of copper must be weighed the moment the crucible is cold enough to be put into the scale, the crucible having, upon removal from the lamp, been closely shut with a cover. The deutoxide of copper attracts moisture very eagerly.

The more diluted the solution of deutoxide of copper, the more complete its precipitation b[illegible]tic potash.

and the oxide of zinc. The solution is filtered, and the precipitate is washed with a solution of muriate of ammonia. It is then dried, and ignited. During the ignition, the peroxide of uranium is reduced to protoxide. This protoxide is digested in dilute muriatic acid, in which, after having been ignited, it is no longer soluble. The substance remaining undissolved after digestion, is, therefore pure protoxide of uranium. The muriatic acid contains in solution the oxides of cobalt, zinc, and nickel, together with a small portion of peroxide of uranium, which, being in a state of combination with those bases, escaped the reducing effect of the ignition. From this solution, the small quantity of peroxide of uranium is now precipitated, with the other metallic oxides, by caustic ammonia. The precipitated oxides are redissolved in muriatic acid, and are again precipitated by ammonia. The precipitate is washed with a solution of muriate of ammonia, and afterwards dried, and ignited. The remaining oxides are estimated in the manner which has been already described.

Separation from the Oxides of Iron.—The oxides of iron are separated from those of uranium as follows: If the protoxides of both metals be present, the first operation is to convert them by nitric acid into peroxides. An excess of carbonate of ammonia is then added to the solution. This dissolves the peroxide of uranium, and precipitates the peroxide of iron.

Separation from Protoxide of Manganese, the Earths, and the Alcalies.—The oxides of uranium are separated from protoxide of manganese and magnesia, in the same manner as from oxide of cobalt. The peroxide of uranium cannot be separated from magnesia by bihydrosulphuret of ammonia, because the sulphuret of uranium is not quite insoluble in an excess of bihydrosulphuret of ammonia.—Peroxide of uranium is separated from alumina, in the same manner as from peroxide of iron.—Lime and strontian can be separated from peroxide of uranium as follows: The solution is mixed with sulphuric acid and alcohol: sulphate of lime and sulphate of strontian are precipitated. The precipitate is filtered, and edulcorated with alcohol. The sulphate of peroxide of uranium remains in solution.

provided a sufficient quantity of alcohol has been added. After the evaporation of the alcohol, the peroxide of uranium is precipitated by ammonia.—From barytes, the peroxide of uranium is separated by sulphuric acid, which throws down sulphate of barytes.—To separate peroxide of uranium from the fixed alcalies, an excess of caustic ammonia is added to the solution. The resulting precipitate is washed with a solution of muriate of ammonia. The fixed alcalies are separated from the filtered solution.

XXII. COPPER.

Precipitation by Caustic Potash.—The best reagent for precipitating the deutoxide of copper is caustic potash. The solution containing the deutoxide of copper is heated in a porcelain capsule, or, what is better, in a platinum capsule; it is carefully brought to the boiling point, and while boiling, is mixed with a solution of caustic potash: thereupon the deutoxide of copper forms a heavy brownish black precipitate. If the precipitation of the deutoxide of copper be effected in the cold, it produces the hydrate of deutoxide of copper, which forms a bulky blue precipitate. This hydrate, however, when boiled, becomes denser, and of a brownish black colour, and is converted into deutoxide of copper. The deutoxide of copper is washed clean with difficulty; the washing succeeds best with hot water, because this is capable of completely dissolving the last traces of potash. When the precipitate is dry, it must be ignited. The ignition can be very well performed in a platinum crucible. The filter is burnt with the precipitate. If any of the deutoxide of copper should thereby be reduced to protoxide, the latter easily reoxides itself in the current of air produced during the ignition. The deutoxide of copper must be weighed the moment the crucible is cold enough to be put into the scale, the crucible having, upon removal from the lamp, been closely shut with a cover. The deutoxide of copper attracts moisture very eagerly.

The more diluted the solution of deutoxide of copper, the more complete its precipitation by caustic potash.

When the solution is very concentrated, there remains, after precipitation by caustic potash, traces of copper still in solution; and if the liquid be mixed with bihydrosulphuret of ammonia, it is rendered very brown. This is not the case, when, previous to the addition of the potash, the solution of deutoxide of copper is diluted with a large quantity of water.

Separation from Nitric Acid.—When the deutoxide of copper is dissolved in nitric acid, or when the solution of deutoxide of copper contains nitric acid, the deutoxide of copper is not always completely precipitated by caustic potash; there generally remains a small portion of copper in solution, even when a very great excess of potash has been added. When, therefore, the object is to separate deutoxide of copper from a nitric acid solution by means of potash, it is necessary, first to add sulphuric acid to the solution, and by the help of heat, to decompose and expel the nitric acid. The heat applied must be gentle, and the evaporation carried on nearly to dryness. When the whole of the nitric acid has been driven away, the solution ceases to give the acid vapours, which denote its presence. The sulphate of copper and excess of sulphuric acid are then mixed with a large quantity of water, and the deutoxide of copper is precipitated from the warm solution by caustic potash.

Separation from Ammonia.—When deutoxide of copper is held in solution by an excess of ammonia, it can be completely precipitated by boiling with caustic potash, even when nitric acid is present.—It would be possible, therefore, if one had a solution of deutoxide of copper and nitric acid, to prepare it for precipitation by caustic potash, by previous supersaturation with ammonia. It is better, however, to expel the nitric acid by sulphuric acid, in the manner described above.

Precipitation by Carbonate of Potash.—Deutoxide of copper must not be precipitated by carbonate of potash; for the precipitation is incomplete, and the copper which remains in solution can only be obtained by evaporating the solution to dryness, and exposing the salt to a gentle ignition.

Precipitation by polished Iron.—The precipitation of metallic copper from solutions of deutoxide of copper, by means of polished iron plate, is a method which never gives an accurate result. The metallic copper becomes partially oxidised during the drying, and is, moreover, generally mingled with charcoal, which the iron deposits on dissolving.

Precipitation by Sulphuretted Hydrogen Gas.—Deutoxide of copper can be very easily separated from all metallic oxides whose acid solutions afford no precipitate with sulphuretted hydrogen gas. The solution of the deutoxide is acidulated by muriatic acid, and subjected to the action of a very slow current of sulphuretted hydrogen gas. This operation is continued until the liquid is quite saturated with sulphuretted hydrogen, and gives a strong smell, when the gas is no longer passed into it. The precipitated sulphuret of copper must be immediately filtered and washed, and the washing must be completed at once, and not be interrupted. If not filtered soon, the sulphuret of copper very quickly becomes oxidised in the cold, especially if nitric acid be contained in the solution. It is, therefore, absolutely necessary, that the solution smell continually of sulphuretted hydrogen gas during its filtration. The quantity of deutoxide of copper contained in the solution cannot be well calculated from the weight of the sulphuret of copper, because the latter becomes partially oxidised during its drying in the air. In consequence of this circumstance, it is necessary to convert the sulphuret of copper into deutoxide of copper, and to determine the weight of the latter.

Conversion of Sulphuret of Copper into Deutoxide of Copper.—The sulphuret being washed and still wet, is removed, with the filter, from the funnel into a glass. The operator pours over it nitric acid or aqua regia, and allows it to digest, assisted by a gentle heat, until all the copper is dissolved, and the insoluble sulphur has a clear yellow colour. This oxidation is much more easily effected by aqua regia than by nitric acid alone. Having separated the sulphur by filtration, and washed it well, the operator adds sulphuric acid to the solution, and evaporates it until the nitric acid is entirely expelled. The remainder, consisting of sulphate of deutoxide of copper and the excess of sulphuric acid, is then treated with a large quantity of water, and the deutoxide of copper is precipitated from the diluted and warm solution by caustic potash.

Precipitation by Bihydrosulphuret of Ammonia.—Deutoxide of copper, contained in neutral or ammoniacal solutions, can be completely precipitated by bihydrosulphuret of ammonia. The precipitated sulphuret of copper is perfectly insoluble in every excess of ammonia or bihydrosulphuret of ammonia. On exposure to the air, it becomes oxidised much sooner than the sulphuret of copper produced by precipitation from an acid solution by sulphuretted hydrogen gas. It must, in consequence of this, be washed with water, to which a little bihydrosulphuret of ammonia has been added. After being washed, it must be oxidised by nitric acid or aqua regia, and the deutoxide of copper must be precipitated by caustic potash.

Separation from Peroxide of Iron by Ammonia.—On account of the ready solubility of deutoxide of copper in ammonia, this reagent has been employed to separate deutoxide of copper from substances which ammonia completely precipitates. Deutoxide of copper is often separated in this manner from peroxide of iron. The peroxide of iron which is thus precipitated contains, however, a considerable quantity of deutoxide of copper, which cannot be dissolved by any excess of ammonia. The separation by sulphuretted hydrogen gas is, therefore, much preferable to this method.

Separation from Oxide of Zinc by Potash.—Oxides which are soluble in a solution of caustic potash, are still often incapable of being separated from deutoxide of copper by this reagent. Thus, for example, it is impossible, even by the employment of the greatest excess of caustic potash, to separate deutoxide of copper from oxide of zinc. It is true, that we can hereby completely precipitate the deutoxide of copper, but it so happens, that a portion of oxide of zinc falls with it, and contaminates it. It would, therefore, be to commit a great fault, if, in the quantitative examination of brass, the operator were to treat its solution, as is often recommended, by caustic potash. The separation of oxide of zinc from deutoxide of copper is perfectly and easily effected, by passing a current of sulphuretted hydrogen gas through an acidulated solution of the two oxides.

Separation from the Oxides of Uranium, Nickel, Cobalt, Iron, Manganese, and Zinc, and from the Earths and Alcalies.—By sulphuretted hydrogen gas, passed into acidulated solutions, deutoxide of copper can be precipitated from the oxides of uranium, nickel, cobalt, iron, and manganese. Deutoxide of copper can also be separated from oxide of zinc by sulphuretted hydrogen gas; but in this case, the solution must be made more strongly acid, in order to prevent the precipitation of sulphuret of zinc with the sulphuret of copper. Sulphuretted hydrogen gas can also be employed to separate deutoxide of copper from the earths and alcalies.

Separation from Oxide of Bismuth.—The best method of separating deutoxide of copper from oxide of bismuth is by means of carbonate of ammonia, which, on being added in excess, dissolves the deutoxide of copper, and precipitates the oxide of bismuth. The operator must not filter the solution immediately after adding the carbonate of ammonia, but must allow the whole to remain for some time in a warm place, that the oxide of bismuth may fully deposit itself. It is good to pour a solution of carbonate of ammonia over the oxide of bismuth while still wet on the filter. This assists the final separation of the deutoxide of copper, which, however, is not easily effected. The precipitate is afterwards ignited and weighed. The filtered solution is gently evaporated to expel the excess of carbonate of ammonia. A little caustic ammonia is then added, and the deutoxide of copper is precipitated by caustic potash.

Separation from Protoxide of Lead.—The separation of deutoxide of copper from protoxide of lead, is best effected as follows: Both oxides are dissolved in nitric acid; the solution is mixed with sulphuric acid, and evaporated to dryness; and the dry mass is heated sufficiently to expel the excess of sulphuric acid. Water is then poured over the fixed remainder, and sulphate of lead remains undissolved. It is filtered and washed, then dried, and gently ignited. From the filtered solution, deutoxide of copper is precipitated by caustic potash. A very small quantity of sulphate of lead dissolves in the water with the sulphate of copper, and escapes precipitation by the excess of caustic potash. This sulphate of lead remains in the solution filtered from the precipitated deutoxide of copper. So much of an acid is added to the solution, that the liquid remains but very weakly alcaline. A little oxalate of ammonia is then applied. Thereupon, the small portion of protoxide of lead precipitates in the state of oxalate. This salt is ignited, and thus converted into protoxide of lead. Every solution, which contains these two metals, is to be treated in a similar manner. It is all the better, however, when the solution contains no ammoniacal salts, because the expulsion of the sulphate of ammonia is attended with difficulties.—A more accurate result is obtained by following this method, than by separating deutoxide of copper and protoxide of lead, by carbonate of ammonia. The precipitated carbonate of lead, even when a great excess of carbonate of ammonia has been employed, always contains a little deutoxide of copper, which colours it greenish. If a solution of carbonate of ammonia is poured upon the carbonate of lead while it is upon the filter, it redissolves, indeed, a portion of the deutoxide of copper, yet it is extremely difficult to free the carbonate of lead wholly from deutoxide of copper.

Separation from the Oxide of Cadmium.—According to STROMEYER (SCHWEIGGER'S Jahrb. T. XXI. p. 301), deutoxide of copper is separated from oxide of cadmium by carbonate of ammonia, which must be added in excess. Hereupon, carbonate of cadmium precipitates, while deutoxide of copper, with a little oxide of cadmium, remains in solution. When this solution is exposed to the air, the oxide of cadmium first deposits itself almost completely; the carbonate of ammonia flies away, and the deutoxide of copper remains in solution.

XXIII. SILVER.

Precipitation as Chloride of Silver.—Oxide of silver can be separated from other substances, and quantitatively estimated, with more ease and greater accuracy than most other oxides. The oxide of silver is precipitated from its solutions by muriatic acid, in the state of insoluble chloride of silver. In the effecting of this precipitation, no other precautionary measure is to be observed than that of acidulating the solution before precipitating the chloride of silver, by the addition of a little nitric acid. In a neutral solution, the chloride of silver does not properly subside; and ammoniacal, the solution must not remain on any account; for, if an excess of ammonia be present, no chloride of silver can be precipitated. When the operator has a strongly concentrated solution of silver, he must not precipitate it with very strong muriatic acid, because an excess of muriatic acid is capable of dissolving a little chloride of silver, which, however, mere dilution with water is sufficient to precipitate completely.

It is more accurate to precipitate silver by muriatic acid than by solutions of chloride of potassium, chloride of sodium, or of muriate of ammonia; for the latter, and particularly the muriate of ammonia, is capable of retaining traces of chloride of silver in solution. This is particularly the case when it is added in large quantity. When, in the precipitation of chloride of silver, the presence of much muriate of ammonia, chloride of potassium, or chloride of sodium, is unavoidable, a case which can readily occur, the most advisable mode of procedure, according to GAY-LUSSAC and LIEBEG (Annales de Chimie, T. XXV. p. 289), is to evaporate the solution filtered from the chloride of silver nearly to dryness, and to treat the remainder with nitric acid. If the whole be then exposed to heat, the alcaline chlorides are converted into nitrates, while the small quantity of chloride of silver remains unaltered, and does not dissolve when the mixture is diluted.

Before the operator filters the precipitated chloride of silver from the solution, it is good to expose the whole to a moderate heat, as the chloride of silver then subsides better. After filtration, he must at first wash the precipitates with water that has been very weakly acidulated by nitric or muriatic acid. For, if it were to be treated at once with pure water, a portion of the chloride of silver would pass through the filter, and produce a cloudiness in the filtered solution. Subsequently, the water passes clear through the filter. It does not always happen that the chloride of silver passes through the filter and forms a milky solution with the wash-water; but the operator has it always in his power to prevent it, by weakly acidulating the water.—The chloride of silver, after being washed, must be very well dried, and then transferred to a weighed porcelain crucible. The filter must be cleaned as completely as possible from the precipitate, burnt to ashes upon the cover of a crucible, and then added to the precipitate. The little porcelain crucible must then be closed with the cover upon which the filter has been burnt. The chloride of silver is then to be fused, allowed to cool, and weighed. If the chloride of silver is not, in the first place, perfectly freed from all moisture by drying, it is liable to spirt about during the fusion, and so occasion a loss. From the weight of the resulting chloride of silver, the quantity of silver, or oxide of silver, is calculated.

Separation by Muriatic Acid from all the Oxides hitherto treated of.—By muriatic acid, the oxide of silver can not only be completely precipitated from its solutions, but separated also from all the oxides which have hitherto been treated of; for the metals of these oxides form compounds with chlorine, which are all soluble in water. Even protoxide of lead can be very well separated from oxide of silver by muriatic acid. But it is then proper to dilute the solution with a very large quantity of water, previous to adding the muriatic acid, because the chloride of lead is but difficultly soluble in water.

Precipitation as Sulphuret of Silver.—Oxide of silver can be completely precipitated from acid solutions by sulphuretted hydrogen gas, and from ammoniacal solutions by bihydrosulphuret of ammonia. It is customary, however, to precipitate oxide of silver in this manner, only when it is to be separated from substances which have to be taken into consideration farther on. Nevertheless, it can be extremely well separated by sulphuretted hydrogen gas from the oxides of uranium, nickel, cobalt, zinc, iron, and manganese, as well as from the earths and alcalies. The solutions must, in all cases, be acid. The sulphuret of silver thrown down by sulphuretted hydrogen gas, can be filtered on a weighed filter, then dried and weighed; after which, the quantity of silver can be reckoned. If, however, the operator believes that the sulphuret of silver is accompanied by sulphur, which will be the case when it has been precipitated from a solution containing peroxide of iron, then he must digest it, with the filter, in nitric acid, until the separated sulphur has a pure yellow colour. He must then filter the solution, and precipitate the silver by muriatic acid, as chloride of silver.—The sulphuret of silver thrown down by bihydrosulphuret of ammonia, must invariably be treated in this manner.

Analysis of Alloys of Silver by Solution.—If the operator desires to analyse alloys of silver with other metals, in the wet way, he can either first dissolve them in nitric acid, and precipitate the oxide of silver from the solution by muriatic acid, or he can treat the alloy directly with aqua regia, whereupon, after diluting the solution with water, the chloride of silver remains undissolved. It is better, however, first to dissolve the metals in nitric acid, and then to treat the solution with muriatic acid.

Analysis of Alloys of Silver by Cupellation.—In order to determine the quantity of silver in many alloys, in those namely, in which silver is combined with copper, lead, or with other base metals, an operation, which is termed cupellation, is commonly made use of. Cupellation consists essentially in this: The base metals which are combined with the silver, and a portion of lead which is added for the purpose, become oxidised by the heat and the air which is allowed to have access. These oxides of the base metals combine together, and constitute a fusible mass, which sinks into the pores of the cupel, a little vessel employed to contain the mixture. The silver alone remains behind in the reguline state, and after cooling, can be quantitatively estimated. The quantity of the other metals contained in the alloy, cannot, in this manner, be determined. As this process, with all the precautionary measures which are to be observed, is very accurately described in a great many good chemical and technical books, the circumstantial description of it may be passed over here; the more especially, as the process cannot be employed in very accurate quantitative determinations, for, in accuracy, it stands far behind the separation of silver in the wet way.

XXIV. MERCURY.

Quantitative Estimation by Reduction.—The best way to determine the quantity of mercury in analysis, is to reduce it to the metallic state, whatever may be the state in which it exists in solution. The best reducing agent is the protochloride of tin. But the reduction of mercury can also be effected by a solution of phosphorous acid, or by the acid which is produced by the deliquescence of phosphorus in moist air. As the protochloride of tin, however, can be obtained in large quantities much more easily than phosphorous acid, so the protochloride of tin is commonly made use of. It is a matter of indifference whether the mercury exists in solution, as peroxide, protoxide, or chloride. The solution may contain free muriatic acid, diluted sulphuric acid, or any other acid; only, it dare contain no nitric acid. If nitric acid be present in the mercurial solution, then peculiar measures of precaution have to be observed. It is in no case, however, a matter of necessity that the mercurial compound to be analysed, should be soluble in water or in muriatic acid; for the mercury can be most completely reduced to the reguline state by protochloride of tin, even when existing in the insoluble salts of peroxide or protoxide of mercury, or in the insoluble chlorides, &c.

Reduction by Protochloride of Tin.—The methods employed to effect the reduction are as follow: When the mercurial substance is insoluble, the operator places it in a matrass, pours concentrated muriatic acid upon it, and then adds a concentrated solution of protochloride of tin, to which he has previously added a sufficient quantity of muriatic acid, to render it perfectly clear. The whole is then boiled, but the boiling dare be continued for only a very few minutes; for, during a long boiling, vapours of mercury might be volatilized in company with the aqueous vapour. The operator now corks the matrass, and suffers all to cool. The mercury is then completely reduced; at first, it is deposited in the state of a black precipitate, consisting of finely-divided globules of mercury; during the boiling, these unite into larger globules. When the matrass is cold, the operator pours off the clear solution, and washes the globules of mercury, without employing filtration, with water acidulated by a little muriatic acid, until the mercury is entirely freed from all extraneous and soluble substances. The wet mercury is then shaken into a little counterpoised platinum or porcelain crucible, and as much as possible of the water which rises above the mercury is absorbed by bibulous paper. After this is done, the mercury must be fully dried and weighed. The drying must be effected by the action of the air alone; the crucible dare not be placed in a warm situation, however gentle the degree of heat might be.—If the black precipitate of globules of mercury will not unite into larger globules, the liquid must be decanted, and the precipitate be boiled for a few minutes with muriatic acid, upon which, larger globules will immediately make their appearance. It very often happens, that layers of minute globules of mercury swim on the surface of the solution: the operator must endeavour to wet these on the surface by swinging the solution: they will then fall to the bottom. The liquid decanted from the reduced mercury, must, with the wash-water, be poured into a glass. This mixture often gives traces of reduced mercury, which have remained in suspension in the solution. The portion of mercury so obtained, must be carefully added to the principal quantity.

Reduction from diluted Solutions.—When mercury is contained in a diluted solution, the solution must be acidulated by muriatic acid, and mixed with a solution of protochloride of tin, previously rendered clear by the addition of muriatic acid; the whole must then be boiled during a few minutes. In this case, the mercury forms only a black

black precipitate, and seldom unites into large globules. The operator separates the clear solution, pours concentrated muriatic acid upon the mercury, and applies heat: large globules of mercury then appear immediately. The black precipitate must not be allowed to repose more than twenty-four hours; for, after that time, no large globules of mercury can be produced by treating the precipitate with muriatic acid. The reason that the large globules of mercury do not directly form in the diluted solution, is, that a small quantity of peroxide of tin falls down with the reduced mercury, and prevents its formation into globules. This peroxide of tin is dissolved by the concentrated muriatic acid; yet, when the mixture has been allowed to repose too long, the solution of the peroxide of tin can scarcely be effected.

Reduction from Nitric Acid Solutions.—The determination of mercury in this manner becomes uncertain, when the solution contains nitric acid. It is then necessary to add muriatic acid gradually to the solution, and to concentrate it by evaporation. The nitric acid is thereby destroyed, free chlorine being, in the mean time, disengaged by the muriatic acid. So long, therefore, as a fresh addition of muriatic acid to the heated solution, occasions the odour of chlorine to be produced, the addition of the muriatic acid must be continued. The operator afterwards pours a solution of protochloride of tin into the mixture, and proceeds in the manner which has been described above. When the solution contains nitric acid in considerable proportion, it is very difficult, even when the greatest precaution is taken, to obtain the right quantity of mercury. It is only when the nitric acid is contained in a solid mercurial compound, that it is easy to destroy the nitric acid by concentrated muriatic acid.

Reduction by Phosphorous Acid.—If the operator intends to apply phosphorous acid, or the acid produced by the deliquescence of phosphorus, to the reduction of mercury, he has to operate nearly in the same way as if he were to employ protochloride of tin. The large globules of mercury are much easier produced by these acids than by the tin salt. The phosphorous acid can also be directly added to a solution containing nitric acid, provided only a sufficient excess of it be employed; for the nitric acid is more effectually destroyed in the heat by phosphorous acid than by muriatic acid. Indeed, the use of the phosphorous acid would, on this account, be preferable to that of the protochloride of tin, were it but possible to procure this acid in large quantities, with the same ease that the tin salt can be procured.

Separation of Mercury by Distillation, &c.—The quantity of mercury contained in a substance submitted to analysis is determined in the best and most accurate manner by reduction. Other methods of determining the quantity of mercury effect the object very incompletely. The peroxide of mercury may, for example, be precipitated from solution by alcalies; but the precipitation is always imperfect.—The quantity of mercury existing in a compound is often estimated by separating it from the other constituents by distillation. This method, however, requires a great deal of care, and affords, when even the greatest precaution is taken, less accurate results than the reduction by means of protochloride of tin. The mode of operating is as follows: The mercurial substance is weighed in a little retort, and then, if the mercury be present in the state of oxide, of oxygen salt, or of sulphuret, it is mingled with carbonate of potash or with pure lime. The potash attacks the glass too powerfully; on which account, the lime is preferable: it is best, however, to employ lime and potash together; but it is first, always, to be considered, whether any of the constituents of the remainder are to be quantitatively determined. When the mixture is made, the neck of the retort is drawn out to a fine tube, which, however, must not be too thin. The point is then led into a receiver, which must contain such a quantity of water that the mouth of the retort may be close over its surface. Were the neck of the retort barely inserted into the water, the latter would rise into the retort, if the heat applied to effect the distillation should happen to be diminished during only a single instant. If the retort be very small, the distillation may be performed over a spirit lamp with circular wick. It is better, however, to make use of a small furnace; but the operator must then take care, not to employ so strong a heat as to melt, or even to soften the glass. The distilled mercury is found at the bottom of the receiver, under the water. If the receiver has been cooled on the outside during the operation, there is no reason to fear that a ponderable quantity of mercury will have escaped from the receiver in vapour. After becoming cool, the neck of the retort is cut off near the body, and the globules of mercury which it contains are washed into the receiver with water. The mercury is then dried in the air, and weighed.—If the mercurial compound is very volatile—if, for example, it contains calomel or corrosive sublimate—it then happens almost invariably, that a portion of it is driven away by the heat before the alcaline substance has been able to effect the decomposition; this is particularly the case when the two substances have been imperfectly mingled. It is better, therefore, when a very volatile mercurial compound is to be decomposed, after having mixed it with the alcali, to moisten it thoroughly with water, and allow the whole to repose for some time. This effects a decomposition, and peroxide of mercury is produced, which the subsequent application of heat resolves at once into mercury and oxygen. The volatilization of the compound in an undecomposed state, need not be anticipated when the mercury is present in the state of peroxide or sulphuret.—It has been already observed above, that the quantity of mercury contained in a compound, cannot be so accurately determined by the distillation, as it can by the reduction, of the mercury.

Analysis of Amalgams.—When mercury is combined in a metallic compound with metals which are not volatile, the quantity of the mercury can often be accurately determined by subjecting the amalgam to ignition: thereupon, the mercury volatilizes, while the fixed metals remain behind: the quantity of the latter is then determined by weight, but the quantity of the mercury is estimated from the loss. If the metals which remain behind do not become oxidised in consequence of exposure to the air, the ignition may be performed in a small porcelain crucible, over the spirit lamp with circular wick; but if, on exposure to a high temperature in contact with the air, the remaining metals are liable to alteration, the ignition must be performed in a small retort, the neck of which, after the volatilization of the mercury, must be closed by the blow-pipe, while the retort is still ignited.

Precipitation by Sulphuretted Hydrogen Gas, and Separation from the Oxides of Uranium, Nickel, Cobalt, Zinc, Iron, and Manganese, and from the Earths and Alcalies.—Mercury can be completely precipitated from its solutions, whether it be contained therein as peroxide, protoxide, or chloride, and even when the solutions are acid, by sulphuretted hydrogen gas. The oxides of mercury can thus be separated from the oxides of uranium, nickel, cobalt, zinc, iron, and manganese, as well as from the earths and alcalies, since none of these bodies can be precipitated from acid solutions by sulphuretted hydrogen gas. In solutions of protoxide of mercury, an immediate precipitate of sulphuret of mercury is formed; but in solutions of peroxide and perchloride of mercury, the pure black sulphuret of mercury is only formed when the current of sulphuretted hydrogen gas has been passed through during a considerable time. In the beginning of the experiment, white-coloured compounds of mercurial salts with sulphuret of mercury, are produced; an additional quantity of sulphuretted hydrogen gas, however, converts these compounds into sulphuret of mercury. If the operator knows to a certainty, that the solution contains only peroxide or chloride, and no portion of protoxide, he can readily calculate the quantity of mercury from the weight of the resulting sulphuret. But, in that case, there dare not have been any peroxide of iron in the solution; for the sulphuret of mercury will then be accompanied by free sulphur. The resulting sulphuret of mercury is filtered on a weighed filter, and dried by the application of a very gentle heat, until, after repeated weighings, it is no longer found to diminish in weight. The sulphuret of mercury in minimum of sulphur, precipitated by sulphuretted hydrogen gas from solutions of protoxide of mercury, cannot be estimated with such accuracy; for it is liable to be partly decomposed, even by a very gentle heat, into sulphuret of mercury in maximum of sulphur, and metallic mercury. And as, now, the metallic mercury is known to be partially volatilized, when exposed to even a very gentle degree of heat, so the precipitate of sulphuret of mercury in minimum of sulphur, is invariably found to diminish continually in weight, when exposed to heat for the purpose of being dried, although the heat applied may be extremely moderate.

Reduction of Sulphuret of Mercury.—If the operator be not quite sure that the sulphuret of mercury he has obtained by precipitation with sulphuretted hydrogen gas is perfectly pure, or if he is unwilling to estimate the quantity of mercury from the weight of the sulphuret, then, an additional operation is necessary. The best method of examining the sulphuret of mercury, is the following: The sulphuret of mercury is gathered and edulcorated upon a small filter of thin paper. It is transferred while still wet, with the filter, into a pretty large flask, which must have a rather wide mouth, and yet be capable of being closed by a glass stopple. The operator pours over it a very small quantity of diluted muriatic acid, i. e. as much as occupies about the twelfth part of the capacity of the flask. He then leads into the solution, a slow current of chlorine gas, by which the sulphuret of mercury is gradually but completely decomposed. The mercury combines with the chlorine and forms perchloride of mercury, which dissolves in the liquid: a portion of the sulphur is converted, in the mean time, into sulphuric acid, while another portion remains undissolved. The whole of the sulphur could, however, be made to dissolve, by continuing to pass the chlorine gas into the solution, during a much longer time. But the addition of chlorine is put an end to, when it is observed that the undissolved sulphur has a clear yellow colour. The tube for conducting the gas is removed from the liquid, and very carefully washed with water. The flask is then exposed to a very gentle digesting heat, till the free chlorine is expelled. After cooling, the solution is filtered from the sulphur; the latter is washed, and the mercury is reduced from the filtered solution by protochloride of tin.

Separation from Nitric Acid, by Sulphuretted Hydrogen Gas.—This method can also be employed when the mercurial solution contains a considerable quantity of nitric acid, a case in which, as has been observed above, the immediate estimation of the mercury by means of protochloride of tin is inaccurate. The nitric acid solution is subjected to the action of sulphuretted hydrogen gas, and the resulting sulphuret of mercury is treated in the manner just described.

Precipitation by Bihydrosulphuret of Ammonia.—Mercury can be fully precipitated, but only in the cold, from neutral or alcaline solutions, by bihydrosulphuret of ammonia. An excess of the precipitant does not dissolve the precipitate in the cold. It is proper, however, to treat the sulphuret of mercury thus obtained with chlorine gas, and to reduce the mercury from the solution of perchloride of mercury, by means of protochloride of tin. To reckon the quantity of mercury from the weight of the sulphuret of mercury, is a method that gives a less accurate result.

Separation from Oxide of Silver.—Peroxide of mercury is fully separated from oxide of silver by muriatic acid, which precipitates the silver alone. The solution is filtered from the chloride of silver, and the mercury is either immediately precipitated by protochloride of tin, or if too much nitric acid is present, is first subjected to the action of sulphuretted hydrogen gas.—When a compound of protoxide of mercury and oxide of silver is to be analysed, the protoxide must first be converted into peroxide. This oxidation is, in most cases, effected by digesting the dry substance, or its solution, with nitric acid; heat being applied to the mixture.

Separation from the Oxides of Copper.—The oxides of mercury are best separated from the oxides of copper by the process which follows: The solution is diluted, and sulphuret of copper and sulphuret of mercury, are precipitated by a stream of sulphuretted hydrogen gas. When mercury is present in the state of protoxide, it is previously necessary to convert it into peroxide. The resulting sulphurets are filtered, and rapidly edulcorated, on a weighed filter; they are then cautiously dried by a very gentle heat, and weighed. It is still better, not at first to warm the sulphurets, but to dry them, with the filter, over sulphuric acid, under the receiver of an air-pump. When they have been thus completely dried, they should be very gently warmed, and then weighed. By drying the precipitate under the receiver of the air-pump, the operator prevents the oxidation of a small portion of the sulphuret of copper, which is unavoidable when the moist precipitate is dried in contact with the atmosphere.—A sufficient quantity of the dried sulphurets is now brought into a small glass bulb, which has a glass tube joined to each side. The glass apparatus is first weighed empty; the sulphurets are inserted, the tubes are carefully cleaned with the plume of a feather, and the glass is once more weighed with its contents: the operator thus learns the quantity of the sulphurets employed in the experiment which follows: Gaseous chlorine is produced, and is led over the sulphurets. The same apparatus is employed, that has been figured and described at page 77. In the flask *a*, however, instead of chloride of sodium, a mixture of chloride of sodium and peroxide of manganese must be placed. This mixture yields chlorine gas, when the operator gradually pours into the flask, by the funnel *b*, a mixture formed of concentrated sulphuric acid, with about an equal volume of water. The gaseous chlorine is perfectly freed from all moisture by the chloride of calcium in the tube *d*. When the whole apparatus is filled with chlorine, the operator applies a very moderate heat to the sulphurets in the bulb *e*. The first compound disengaged is chloride of sulphur, which flows into the flask and is decomposed by the water, a deposition of sulphur taking place. The metals also combine with the chlorine, and the volatile perchloride of mercury can be completely separated from the chloride of copper by the application of heat. Not far from the bend of the glass tube, a sublimate of slender crystals, consisting of perchloride of mercury, is observed. These crystals are so abundant, that a glass tube of very small diameter would soon be obstructed by them. The operator continually drives them onward from the bulb *e*, by applying the flame of a small spirit lamp; and when no new crystals are sublimed, he ceases to heat the bulb *e*. When the apparatus is quite cold, the part of the glass tube which contains the sublimate is cut off with a file, and the sublimate is washed with water into the flask, in the liquid of which the crystals dissolve. The flask is then closed with the glass stopple, and is placed in a moderately warm situation. After being allowed to cool, the insoluble sulphur is filtered from the solution. If the disengagement of chlorine gas has been too long continued, the whole of the sulphur is often dissolved and converted into sulphuric acid. The solution filtered from the sulphur, must be heated in contact with the air, until the smell of chlorine is no longer perceptible. It is unnecessary to heat the solution, when it does not smell of free chlorine. The mercury is then precipitated by a solution of protochloride of tin.—The bulb *e* contains merely the chloride of copper. It is impossible to determine the quantity of copper from the weight of the chloride; the latter being always a mixture of perchloride and protochloride of copper in uncertain proportions. The greater the heat employed to warm the bulb, the greater the quantity of protochloride produced. The glass tube and the bulb *e* are plunged into water, to which muriatic acid has been added. At first, a precipitation of protochloride of copper takes place; but in consequence of the presence of atmospheric air and muriatic acid, the protochloride is speedily converted into perchloride, and when the solution is warmed, the whole dissolves. A solution of caustic potash is then added, and the mixture being heated, the copper is completely precipitated in the state of deutoxide.

The analyst finds in this manner the relative proportions of mercury and copper in the weighed quantity of the mixed sulphurets employed in the experiment. He can consequently ascertain, by calculation, the quantity of the two metals contained in the whole mass of sulphurets, which was gathered upon a weighed filter in the early part of the analysis.

When oxide of copper exists in solution with the oxides of mercury, their quantitative estimation can be effected by a simpler process than the preceding. Both metals are precipitated by sulphuretted hydrogen gas; the sulphurets are dried in a moderately warm place; and then, being put into a retort, the sulphuret of mercury and a portion of the sulphur of the sulphuret of copper, are expelled by heat. Sulphuret of copper in minimum of sulphur remains behind. This is cooled, and weighed. During the cooling, the air should be kept away from it as effectually as possible. The quantity of copper is calculated from the weight of the sulphuret. But in this case, the quantity of the sulphuret of mercury is difficult of determination; on which account, the other method of analysis, though less simple than this, is still preferable.

Separation from the Oxides of Lead, by Sulphuretted Hydrogen Gas.—The oxides of mercury can be separated from the protoxide of lead, in the same manner as from the deutoxide of copper. This method is indisputably preferable to that in which protoxide of lead is separated from the oxides of mercury by means of sulphuric acid. Supposing the oxides of these two metals to have been precipitated from a diluted solution by sulphuretted hydrogen gas, the resulting sulphurets are to be dried. The drying need not be effected in the vacuum of the air-pump, since neither the sulphuret of lead nor of mercury becomes oxidised when dried in the open air, while the contrary is the case with the sulphuret of copper. In decomposing the sulphurets of lead and mercury by gaseous chlorine, care must be taken to apply only a very gentle heat to the bulb *e*, as the application of too strong a degree of heat could effect the volatilization of a portion of chloride of lead in company with the chloride of mercury. It is possible, in this case, to calculate from the weight of the chloride of lead, the quantity of protoxide of lead contained in the substance submitted to analysis. The process is therefore easier than with the chloride of copper. That portion of the glass tube which contains sublimed perchloride of mercury, is cut off. The bulb *e* is then weighed with the chloride of lead it contains. After which, the chloride of lead is dissolved, and the empty bulb is washed, dried, and again weighed. In this manner, the weight of the chloride of lead is found. The equivalent quantity of protoxide of lead is then reckoned.

Separation from the Oxides of Lead by Muriatic Acid.—Supposing the operator to have for examination a dry compound of peroxide of mercury with any one of the oxides of lead, the analysis can be executed by an easier process than the preceding. The compound is treated with muriatic acid, which produces chloride of lead and perchloride of mercury. If the compound contained peroxide of lead, and not the ordinary protoxide, a disengagement of free chlorine takes place. The excess of muriatic acid is expelled by evaporation, for which a very gentle heat is used. The remainder is then treated with alcohol, which dissolves the perchloride of mercury, and leaves the chloride of lead undissolved. This is filtered upon a weighed filter, washed with alcohol, dried, and weighed. The alcoholic solution of perchloride of mercury is mixed with water and evaporated by a very gentle heat, to expel the alcohol; the mercury is then precipitated by protochloride of tin.—When protoxide of lead and peroxide of mercury in solution together, are combined with an acid which can be expelled by muriatic acid, the present method can be also employed in that case. The solution is mixed with muriatic acid, the excess of acid is fully expelled by evaporation, and the residue is treated with alcohol.

Separation from Bismuth and Cadmium.—No accurate methods are known of separating either the oxides of mercury from those of bismuth and cadmium, or metallic bismuth and cadmium from metallic mercury. As the oxides of bismuth and cadmium are not reduced by protochloride of tin or phosphorous acid, it would be possible to estimate by means of these reagents the quantity of peroxide of mercury contained in the substance submitted to analysis. Phosphorous acid is, in this case, to be preferred to protochloride of tin; because the oxides of bismuth and cadmium, contained in the solution filtered from the reduced mercury, must be precipitated by sulphuretted hydrogen gas, and afterwards estimated in the manner which has been described in a preceding section.

Separation of Protoxide of Mercury from Peroxide of Mercury.—When a solution contains both protoxide and peroxide of mercury, and the quantity of each is to be estimated, the solution is mixed with muriatic acid, which precipitates the protoxide in the state of protochloride. The solution must previously be diluted with a large quantity of water, particularly when it is acid. The protochloride of mercury is filtered upon a weighed filter, and dried at an extremely gentle heat, as long as it continues to diminish in weight; the weight of it is then taken, and the equivalent quantity of protoxide of mercury is calculated. The peroxide of mercury, contained in the solution filtered from the protochloride of mercury, is precipitated after one of the methods already described: from the weight of the mercury obtained, the quantity of the peroxide is calculated.—In the precipitation of the protochloride of mercury, the precaution must be observed, especially when nitric acid is present, of diluting the solution with a very large quantity of water; for otherwise, a small portion of the protochloride may be converted into perchloride and remain in solution. Farther, the resulting protochloride of mercury must not be filtered immediately, but allowed to repose some time. But, above all things, the application of heat must be avoided; because, with heat, the addition of muriatic acid alone, is sufficient to convert the protochloride of mercury into the perchloride, the conversion being accompanied by the separation of reguline mercury.

If the substance which contains the protoxide and peroxide of mercury be insoluble in water, it must be treated, in the cold, with very dilute muriatic acid. In most cases, the protoxide of mercury then remains undissolved, in the state of protochloride of mercury. The peroxide at the same time, becomes perchloride and, dissolving in the acid, forms a solution from which the mercury is afterwards reduced. If, however, the insoluble mixture of oxides contains nitric acid, it is good to dissolve it, in the first place, in very dilute nitric acid, and then to add muriatic acid to the solution. If muriatic acid, even in a diluted state, were to be added to a dry substance containing the two oxides of mercury in conformation with nitric acid, then the protoxide of mercury could be dissolved as perchloride of mercury.

XXV. RHODIUM.

Precipitation and Reduction.—When rhodium exists in solution as peroxide or perchloride, it can be best estimated, according to BERZELIUS (POGGENDORFF'S Annal. B. XIII. p. 454), by the process which follows: The solution is mixed with an excess of carbonate of soda, and is evaporated to dryness. The dry residue is then ignited in a platinum crucible. Upon dissolving the mass in water, peroxide of rhodium remains behind, which is brought upon a filter and edulcorated, first with muriatic acid and afterwards with water. It is then ignited with the filter, and subsequently reduced by hydrogen gas. The reduction is very easily effected. The resulting metal is weighed. This reduction by hydrogen gas can be performed in the same manner as the reduction of oxide of cobalt, an operation which has been described at page 82. The reduction of peroxide of rhodium is so readily effected, that it is scarcely necessary to assist the action of the gas by the application of heat.

Separation from other Metals.—It is difficult to separate rhodium from other metals in solution; for although sulphuretted hydrogen gas acts as a precipitant of rhodium, it does not precipitate it fully. Rhodium occurs in nature, however, combined with very few of the substances which have been treated of in the foregoing sections: it is therefore unnecessary to state here, how it could be separated from them.—Rhodium is found only in the ore of platinum; and with respect to the manner in which it is separated from the metals which accompany it, the description of the processes will be given in the article on platinum.

Method of dissolving Rhodium.—Rhodium has been employed of late, to form alloys by combination in small proportions with other metals, for example, with steel. As metallic rhodium is insoluble, even in aqua regia, it might be supposed capable of easy separation from other metals by means of simple acids. Yet in alloys, the rhodium very often exists in such a condition, that it is directly dissolved with the other metals, even by the simple acids; while, on the contrary, it hinders in many cases, the perfect solution of the other metals by acids. To dissolve rhodium with ease, BERZELIUS (POGGENDORFF'S Annalen, B. XIII. p. 452), recommends the employment of bisulphate of potash, with which the rhodium is to be subjected to fusion. During the ignition, the rhodium dissolves, and the dissolution is accompanied by a disengagement of sulphurous acid gas. The dissolution, however, is effected but slowly. The platinum crucible must be closed during the ignition by a cover which shuts well, to check the too rapid volatilization of the excess of acid. As soon as the saline mass becomes fixed and crystalline at the surface when the cover is removed, the crucible must be taken from the fire and cooled. The salt is then dissolved in boiling water, and the undissolved residue is treated with a fresh portion of bisulphate of potash. The melted salt is red and transparent, when it contains but little rhodium; but appears dark and black, when it is nearly saturated with the metal. After cooling, it is either of a dark or bright yellow colour, according as the quantity of rhodium it contains is more or less considerable. By cold water it is slowly, by hot water rapidly, dissolved. The solution is yellow.—So long as the salt continues to receive a colour, the remelting must be repeated. In order to avoid, in analyses, the employment of too great a quantity of bisulphate of potash, the operator may supply sulphuric acid as follows: When the bisulphate of potash appears to have lost the greater part of its free acid, weighed portions of distilled sulphuric acid may be added to the mixture, the whole cautiously heated till the water of the acid is expelled, and the fusion thereupon be continued.

The insoluble residue must always be often remelted with bisulphate of potash in fresh quantities, till the operator has assured himself, by the colourless appearance of the flux, that the salt can dissolve no more rhodium—that no more rhodium is present.—By this process, rhodium can be separated from all metals which are not attacked by bisulphate of potash.

Separation from Copper.—If rhodium and copper be contained in a solution, they may be separated, according to BERZELIUS, in the following manner: The solution is poured into a flask which is furnished with a glass stopple, and is therein saturated with sulphuretted hydrogen gas. The flask is then closed, and allowed to remain for twelve hours in a warm situation. The sulphuret of copper is in that time fully, and the sulphuret of rhodium for the most part, precipitated. The solution is filtered, and being heated and evaporated, yields a fresh portion of sulphuret of rhodium, which is added to the other sulphurets. These are placed, while still moist, in a platinum crucible, and are roasted as long as sulphurous acid is exhaled. When the roasting is finished, the mass is subjected to the action of concentrated muriatic acid; the solution so produced has a green colour, occasioned by the presence of basic sulphate of copper. Peroxide of rhodium remains undissolved. The deutoxide of copper is precipitated from solution by caustic potash.—The liquid filtered from the sulphurets still contains a portion of rhodium. To obtain this, the solution is first freed from sulphuretted hydrogen by heat, and is then treated with carbonate of soda in the manner described above. The resulting peroxide of rhodium is reduced by hydrogen gas, and the metallic rhodium is weighed.

Separation from Iron.—Rhodium occurs not only in combination with copper, but with iron. From the latter, it can, according to BERZELIUS, be separated in the following manner: The greater part of the rhodium is precipitated from the acid solution, by a current of sulphuretted hydrogen gas. The precipitated sulphuret of rhodium is converted by roasting into peroxide of rhodium. The filtered solution is mixed with nitric acid and warmed, to convert the protoxide of iron into peroxide. The peroxide of iron is then precipitated by caustic ammonia. The precipitate is washed, ignited, and weighed. The resulting peroxide of iron still contains rhodium, and the latter exists in this case in such a state, that it is capable of being dissolved with the peroxide of iron by muriatic acid. The peroxide of iron is therefore reduced by hydrogen gas, and the metal is dissolved in muriatic acid, which must at last be warmed. The small portion of rhodium then remains behind, in a condition which has not yet been determined: it is converted, however, by ignition in the open air, into peroxide of rhodium. Its weight is deducted from that of the peroxide of iron, and the quantity of iron is then calculated.—The solution from which the peroxide of iron was precipitated by caustic ammonia still contains a little rhodium. This is obtained by mixing the solution with a sufficient quantity of carbonate of soda, evaporating it to dryness, igniting the residue, and treating it with hot water. The peroxide of rhodium then remains undissolved. The different portions of peroxide of rhodium furnished by the analysis, are mixed together and reduced by hydrogen gas.

Separation from Alcaline Chlorides.—When rhodium, in the state of perchloride, is combined with alcaline chlorides, and is to be quantitatively separated therefrom, the separation can be very easily effected, according to Berzelius (Poggendorff's Annal. B. xiii. p. 439), by the process which follows: A quantity of the chlorides is weighed in an apparatus, such as that described at page 83. It is therein exposed to heat, and to a current of hydrogen gas. The operation is continued until white clouds are no longer produced, when a glass rod, moistened with ammonia, is held at the end of the apparatus where the hydrogen gas escapes. The glass bulb, in which the substance for analysis was placed, is then weighed. The residue is dissolved in water, and the reduced rhodium is filtered, dried, ignited in a current of hydrogen gas, and weighed. The filtered liquor is evaporated to dryness, and the dry mass is ignited and weighed.

XXVI. PALLADIUM.

Precipitation by Cyanuret of Mercury.—Palladium, according to WOLLASTON, can be best precipitated from its solutions, by a solution of cyanuret of mercury. When the solution contains but a small quantity of palladium, the cyanuret of mercury does not produce an immediate precipitate; after some time, however, the solution becomes troubled, and deposits a bright yellow precipitate, which becomes yellowish grey on being dried. After ignition, metallic palladium remains behind, and can be weighed. During the ignition, the palladium becomes blue, but acquires no perceptible increase of weight.—It is necessary to neutralise the solution with soda, should it be acid, previous to adding the cyanuret of mercury.

Precipitation by Sulphuretted Hydrogen Gas.—Palladium can be precipitated from acid solutions by sulphuretted hydrogen gas. It can therefore be thus easily separated from iron and other metals, which are not precipitated from acid solutions by that reagent. The resulting sulphuret of palladium is converted by roasting into basic sulphate of palladium. This salt is dissolved in muriatic acid, and the solution is neutralised by soda and precipitated by cyanuret of mercury. The cyanuret of palladium is then ignited, as was mentioned in the preceding paragraph.

Separation from most other Metals.—Partly by sulphuretted hydrogen gas, but more particularly by cyanuret of mercury, can palladium be separated from nearly all the metals with which it may occur in combination, excepting copper. It is found in company with the latter in crude platinum, and, according to BERZELIUS (POGGENDORFF's Annalen, B. XIII. p. 561), can be separated from it by the following process: Both metals are precipitated from an acid solution by sulphuretted hydrogen gas. The precipitated sulphurets are exposed to heat, while still moist, with the filter, and roasted as long as they give off sulphurous acid. They are thereby converted into basic sulphates of oxides. These salts are dissolved in muriatic acid. The solution is mixed with chloride of potassium and nitric acid, and is then evaporated to dryness. The dark saline mass thus produced contains chloride of potassium, chloride of copper and potassium, and chloride of palladium and potassium. The first two of these salts are to be extracted by alcohol, having the spe. gra. of 0·833. The palladium salt, being insoluble therein, remains behind. It is to be brought on a weighed filter, and washed with alcohol. It is then dried, and weighed. It contains 28·84 per cent. of palladium. The saline mass can also be dissolved in hot water, and submitted to the action of cyanuret of mercury; but this method of estimating the quantity of palladium is less direct than the other. It deserves the preference, however, when the alcohol has too large a quantity of chloride of potassium to extract.—The spirituous solution of the copper salt contains a trace of palladium, which, however, may be altogether neglected. The solution is evaporated to expel the alcohol, and the saline mass is dissolved in water. The copper is then precipitated by caustic potash, and the deutoxide of copper is weighed.

Separation from Alcaline Chlorides.—When palladium is combined, as protochloride, with alcaline chlorides, and is to be quantitatively separated therefrom, the operation is performed in the same manner, as the separation of perchloride of rhodium from alcaline chlorides (page 134). The reduced palladium can, however, be ignited in the open air, and needs not, like the reduced rhodium, to be heated in hydrogen gas.

XXVII. IRIDIUM.

Precipitation by Alcaline Chlorides.—Iridium can, in the following manner, be precipitated from its solutions, and separated from nearly all the metallic oxides which have hitherto been treated of: The solution of Iridium is concentrated. The operator then mixes it with a concentrated solution of chloride of potassium or muriate of ammonia, and adds very strong alcohol in such proportion that the liquid may contain about 60 per cent. of its volume, of alcohol. Thereupon, the chloride of iridium and potassium, or the corresponding compound formed with the ammoniacal salt, both of which are insoluble in alcohol, completely precipitates. The solution must contain a small excess of chloride of potassium. The precipitate is washed with spirits of wine.—Should the operator desire to determine the quantity of iridium in the resulting double salt, then the double salt, which is here supposed to have been precipitated by chloride of potassium, is treated by hydrogen gas, like the double chloride of rhodium and potassium (page 134). If the double salt has been precipitated by muriate of ammonia, then, the direct result afforded by the reduction with hydrogen gas, is metallic iridium, whose weight is estimated. During the reduction, muriate of ammonia and muriatic acid gas are disengaged.

Precipitation by Sulphuretted Hydrogen Gas.—Iridium can be completely precipitated from acidulated solutions by sulphuretted hydrogen gas. The resulting sulphuret of iridium is in a higher or lower state of sulphuration, corresponding with the state of oxidation in which the iridium existed in the solution. The sulphurets are dark-brown or nearly black, and precisely similar in appearance to those furnished by platinum, palladium, and rhodium. They do not become acid while drying. By sulphuretted hydrogen gas, iridium is easily separable from substances which that reagent is incapable of precipitating from acidulated solutions. The resulting sulphuret of iridium dissolves without residue in cold nitric acid, and can be precipitated from this solution, when it is concentrated, by the addition of alcohol and muriatic acid, chloride of potassium or muriate of ammonia.

Separation from other Metals by Bihydrosulphuret of Ammonia.—As the sulphuret of iridium dissolves in bihydrosulphuret of ammonia, it could be thereby separated from several metals whose sulphurets are insoluble in that reagent. When precipitated from such a solution by an acid, the sulphuret of iridium, according to BERZELIUS, is soluble to a certain extent in water, to which it communicates a brownish red colour. The wash-water, therefore, after the acid has passed through, becomes strongly coloured. A great excess of acid, however, prevents the solubility of the iridium; so that, when, by evaporating the liquor, the acid is concentrated, the dissolved iridium gradually precipitates; but the whole cannot be separated in this manner. When the liquor is mixed with a little nitric acid and is then evaporated, the sulphuret of iridium is converted by oxidation into sulphate of iridium.

XXVIII. OSMIUM.

Estimation of small Quantities, as Sulphuret of Osmium.— The quantitative estimation of osmium, is, on account of the volatility of its highest oxide, attended by many difficulties. — If the compound for examination contains osmium in the metallic state, and can be fully dissolved by aqua regia, then the solution is effected in a glass retort, furnished with a receiver. The acid being thereupon carefully distilled over, while the receiver is kept cool, the whole of the osmium is found, at the end of the operation, in the distilled liquor held by the receiver. The quantity of osmium contained in the solution can be determined by different methods. When only a very small quantity of osmium is present, the best process, according to BERZELIUS (POGGENDORFF'S Annalen, B. XIII. p. 555), is the following: The distilled liquor is diluted with water, and saturated to such an extent with ammonia or with some other alcali, that the acid shall still remain somewhat in excess. The solution is then poured into a flask which can be corked, and which the solution is sufficient nearly to fill. A current of sulphuretted hydrogen gas is then driven through, until the solution holds sulphuretted hydrogen in excess. The flask is then corked, and is allowed to repose until the sulphuret of osmium has subsided, which is often not the case till after some days. The clear liquid is decanted or removed by a syphon, and the sulphuret of osmium is brought on a weighed filter, to be washed, dried, and weighed. It contains less osmium than it properly should contain, because it retains a little moisture, and, during the drying, becomes partially oxidised. The proportion of osmium is from 50 to 52 per cent.

Precipitation by Mercury, and Reduction.—When the quantity of osmium in solution is considerable, the best way of estimating it, is, according to BERZELIUS, that of precipitating it by mercury, after having added to the solution so much muriatic acid, that chlorine may be present to combine with the mercury. A precipitate is then produced, which consists of protochloride of mercury, of a pulverulent amalgam of osmium and mercury, and of free mercury containing a very small quantity of osmium. This precipitate is heated in a glass bulb, which has a glass tube soldered to each side, and a current of dry hydrogen gas is allowed to pass over it in the meantime. The volatilised reguline mercury and protochloride of mercury follow the hydrogen gas, while the osmium remains behind, in the form of a porous black powder. This powder does not appear to be metallic, but when it is pressed upon, it exhibits a metallic streak. This metallic osmium is in a state fit for weighing.—The solution, separated from the precipitate, still contains a little osmium. By digestion with mercury, this osmium can be precipitated; but the precipitation is very slowly effected, and requires a tedious digestion. A better method of separating it, is, to saturate the acid with ammonia, to evaporate the solution to dryness, and to heat the mass in a retort. The osmium salt is thereupon decomposed by the ammonia, and the mercury which it may contain is volatilized with the muriate of ammonia, in the state of a double salt.

Separation from other Metals.—In consequence of the volatility of its oxide, it is very easy to separate osmium, by the process of distillation, from the other metals with which it occurs in combination. Iridium, however, with which it forms a native alloy, is an exception to this rule; for these two metals hold together with an obstinacy which may justly be wondered at.

Separation from Iridium.—The analysis of this compound—an analysis in the highest degree difficult—is best effected by the process described by BERZELIUS (POG-

GENDORFF'S Annalen, B. XIII. p. 464). The operator must begin by pulverising it. The compound exists in the form of grains, more or less large, which are extremely hard and possessed of much solidity. They cannot be pounded in a stone mortar, in which the striking of blows sufficiently strong to overcome the resistance of the mineral, would be unsafe. The pounding succeeds best in a mortar of steel, or within a ring upon a steel plate. Such is the hardness of these grains, that, when struck with a blow sufficiently powerful, they force their way into the steel and there remain fixed. After having pounded them as much as possible, the operator must triturate them until the powder is so fine that, when rubbed on the hand, it makes a streak, like graphite. When the grains are once broken into pieces by pounding, the reduction to a fine powder by trituration is effected pretty easily. The labour of trituration must not be *spared;* for it will be found, that the fine powder is afterwards easily decomposed, while the coarse powder is attacked but feebly. The resulting powder is boiled with muriatic acid, which dissolves, under effervescence, the iron abraded from the mortar. The solution of iron is decanted, and the powder is well washed. After that, the washed powder is mixed with an equal quantity, or nearly an equal quantity, of saltpetre, which must, very shortly before, have been melted, to free it completely from water. The mixture is then placed in a small porcelain retort, to which a tubulated receiver has been adapted; a gas-conducting tube must pass from the receiver into a flask containing diluted ammonia. At first, the retort must be heated very gently, and the operator must take care that the disengagement of gas does not proceed with too great rapidity, because, if the action be too violent, the mass in the retort is apt to boil over. Towards the end of the operation, the fire must be so increased as to produce a full white heat. When no more gas is disengaged, the retort is allowed to cool. The contents of the retort are treated with cold water, and the solution is poured into a flask furnished with a ground glass stopple. It is therein mixed with much muriatic acid, and much nitric acid, so as to become extremely acid. It then smells very strongly of osmium. The clear part of the solution is poured into a retort, and submitted to distillation. The operator must take particular care, in this case, to cement the joinings of the apparatus with accuracy, and to keep the receiver as cool as possible. The insoluble portion is likewise treated with muriatic and nitric acids, and is distilled in a separate retort. This distilled liquor also contains osmium, and the residue in the retort contains iridium, with a portion of osmium. The reason that, in this operation, the clear solution is, previous to distillation, separated from the undissolved part, is, to prevent bouncing during the boiling, by which, otherwise, a portion of the solution of iridium could be driven into the receiver. The alcaline solution dare not be filtered through paper, which is found to have a reducing effect upon the oxides which it contains: the paper acquires a green colour from protoxide of iridium, and the solution passes through the filter with uncommon difficulty. The nitric acid is added in excess, that it may decompose the double salt produced by chlorine and osmium, and convert this metal into its volatile peroxide.—The substance, which remains in the two retorts after distillation, is filtered, mixed with chloride of potassium, and evaporated to dryness, to expel the superfluous muriatic and nitric acids. The dry saline mass is well mixed with carbonate of soda, and is then, once more, heated in a retort, as described above, to separate the peroxide of osmium which it may contain. The salt is then dissolved in water, upon which, the peroxide of iridium remains behind. This sometimes contains a little rhodium, to separate which, the peroxide of iridium must be fused with bisulphate of potash, in the manner described at page 132.

After all these operations, however, the iridium still retains a portion of osmium, which adheres to it with surprising firmness. To separate it, the two substances are reduced by hydrogen gas, the action of which is assisted by a very gentle degree of heat. The reduced metals are then kept at a dull red heat in the open air, as long as the odour of peroxide of osmium is perceptible.

In this operation, the iridium must many times in succession be reduced and oxidised, to free it fully from the osmium: the perfect separation, however, is effected very slowly and difficultly. If the iridium be too strongly heated, if, for example, it be raised to a white heat, the two metals again combine together in the most intimate manner, and shrink up: it is then impossible to burn away the osmium.—The weight of the iridium is determined after the last reduction with hydrogen gas. The solutions of osmium produced by the above experiments, are all poured together, and the osmium is separated by the method described above. The small quantity of osmium separated from the iridium, by igniting the latter in the open air, is estimated from the difference in weight found between the iridium when weighed after the first reduction by hydrogen gas and when containing osmium, and when again weighed after the last ignition and last reduction, when freed from osmium.

In the insoluble residue, left upon dissolving platinum ores in aqua regia, the operator not only finds the shining, silver white, crystalline scales of osmium-iridium, which are furnished by some of the platinum ores from the Uralian mountains, but also, according to BERZELIUS, a quantity of rounded grains with irregular surface, which are less rich in osmium than the crystalline scales of osmium-iridium. In the analysis of these grains, other constituents are found besides osmium and iridium. These constituents, it is true, are only mixed with the others, and are unessential to the constitution of the mineral; yet they are mixed therewith in such a manner, that they cannot be readily separated. These constituents are titanic acid, silicic acid, chromic acid, oxide of chromium, zirconia, and peroxide of iron. Their presence evidently proceeds from an intermixture of chromiferous iron, titaniferous iron, and hyacinth; but these substances can neither be distinguished from the grains of osmium-iridium by the eye, nor separated from them by elutriation.

For the analysis of these grains, BERZELIUS recommends a different method from that described above. The mass resulting from the fusion of the pulverised mineral with saltpetre, is mixed with water, that all the saline substances may be dissolved. The mixture is poured into a tubulated retort, in which it is allowed to settle; the solution is then poured off. The residue is treated with a fresh quantity of water, which is likewise decanted when it has become clear. These solutions contain potash-salts of nitric acid, chromic acid, silicic acid, of the second oxide of iridium, and of a small portion of the highest oxide of osmium. By distillation with muriatic acid in a retort, the osmium is completely separated from the other substances. The methods by which the quantitative estimation of the other substances can be effected, will be taken into consideration in subsequent sections.—What remains undissolved in the tubulated retort is mixed with muriatic acid, that every thing may be extracted which muriatic acid is capable of dissolving. The acid solution is then distilled over the water-bath. This operation is continued until a portion of the solution, taken from the retort by the tubulure, has not the least odour of osmium. The distilled liquor is a solution of the highest oxide of osmium in water, containing a little chlorine. The residue in the retort, treated with a small quantity of water, gives a more or less green-coloured solution, the green colour of which is owing to the presence of protochloride of chromium. If the operator now washes the insoluble matter with alcohol, all the protochloride of chromium will be extracted. He will then obtain upon the filter, the double chloride of potassium and iridium. The green solution and the alcoholic liquor, both become troubled upon being diluted with water and heated: a white powder precipitates, which appears like titanic acid, but contains also both silicic acid and zirconia.

Test for Osmium.—To ascertain whether the iridium obtained be quite free from osmium, a very delicate test is presented in the odour produced, when iridium which contains osmium is ignited in contact with air. There is, however, according to BERZELIUS (POGGENDORFF'S Annalen, B. XIII. p. 544), a still more delicate and convenient test, namely, the action of gaseous peroxide of osmium on the flame of the spirit lamp. If an extremely small piece of pure osmium be placed on a slip of platinum foil, near the edge, and be brought into the flame of burning spirits of wine, and held in such a manner as to allow a portion of the flame to rise freely by the side of the platinum, then the flame suddenly becomes very brilliant, just as if pure olefiant gas had been inflamed. If iridium, which contains traces of osmium, be heated in the same manner, a momentary illumination is clearly distinguishable, although the effect is not so striking as with pure osmium. The illumination soon ceases, not because all the osmium is driven away, but because the osmium and iridium become oxidised, and form a fixed compound unsusceptible of higher oxidation. If the operator then pushes the platinum foil so far into the flame, that the metal comes into the inner part of the flame where no combustion is going on, the compound is reduced. It is then again capable of inflaming at the edge of the outer flame, upon arriving at which, it becomes ignited for a moment, and illuminates the flame. Thereupon it can again be raised to a white heat, without giving the odour of osmium, or being at all affected. But after a new reduction, the above phenomena again appear. The power of producing this brilliant light is clearly distinguishable, when the formation of the odour of peroxide of osmium, by the ignition of the reduced metals, is no longer to be perceived with distinctness.

XXIX. PLATINUM.

Precipitation in the state of Reguline Platinum.—Platinum can be precipitated from its solutions, in the reguline state, by a great number of reducing substances. The substance which it is best to employ is mercury, or a solution of protonitrate of mercury. The precipitated platinum contains mercury. The precipitate is washed and dried, then strongly ignited and weighed.

Precipitation by Muriate of Ammonia.—The best method of effecting the quantitative estimation of platinum, is to precipitate it from its solutions as follows: The acid solution of platinum is concentrated, and mixed with a very concentrated solution of muriate of ammonia; so much alcohol is then added as is sufficient to cause the perfect precipitation of the resulting double salt, composed of muriate of ammonia and chloride of platinum. The precipitate is edulcorated with spirits of wine. From the weight of the double salt, it is not easy to determine the quantity of the platinum, because the double salt may contain an excess of muriate of ammonia: the precipitate is therefore ignited, upon which, reguline platinum in a porous state remains behind, and can be weighed. The ignition of this double salt, however, requires, in quantitative analyses, to be conducted with much precaution, since it is very possible for a portion of the finely-divided platinum, to be carried away mechanically with the disengaged vapours. The best plan is, to effect the ignition in a small weighed retort, the neck of which, after having inserted the double salt, and ascertained the quantity by a second weighing, must be drawn out. Care is to be taken, however, not to draw out the neck to too fine a tube, otherwise it may be stopped up by the sublimed muriate of ammonia, and an explosion be produced. In the heating of the retort, only a weak heat must be applied at the beginning, and it must be raised to a red heat very gradually. During the ignition, the operator must endeavour, by means of a little spirit lamp, to drive the sublimed muriate of ammonia as effectually as possible out of the neck of the retort. When the ignition is finished and the apparatus cold, the neck of the retort is cut off, washed clean with water, dried, and weighed with the retort.—Platinum can be precipitated in a similar manner, by the addition of chloride of potassium and alcohol. The precipitated double chloride of potassium and platinum must, in this case also, be washed with spirits of wine. This precipitate can be ignited without loss much more easily than that containing ammonia. Ignition converts it into a mixture of reguline platinum and chloride of potassium. The ignited mass is then treated with water, which dissolves the chloride of potassium, and leaves the platinum untouched. The latter is then ignited, and weighed.—The reduction is effected still better by hydrogen gas, in an apparatus similar to that employed in the reduction of the chloride of potassium and rhodium, as described at page 134.

Separation from Manganese, Iron, Cobalt, Nickel, Copper, Mercury, &c.—By means of proper treatment with muriate of ammonia, or with chloride of potassium, the peroxide of platinum, or rather the perchloride of platinum, can be separated from a great number of metals in solution; namely, from all those whose chlorides are soluble in alcohol. It can thus, for example, be separated from manganese, iron, cobalt, copper, mercury, &c. Should a portion of any other metallic compound be precipitated in company with the compound of platinum, it can be very readily separated from the ignited and reduced platinum, by digestion with nitric or muriatic acid; for neither of these acids can alone attack platinum. Should a little chloride of lead, for example, be precipitated with the platinum compound, the chloride of lead can be partly separated by washing with mere water; but even when a portion of lead has been converted by oxidation into oxide of lead, it can still be entirely separated by digesting the reduced platinum in diluted muriatic acid.

Precipitation by Sulphuretted Hydrogen.—Platinum can be precipitated from acid solutions by sulphuretted hydrogen gas; but the precipitated sulphuret of platinum very easily becomes oxidised in the air. It is possible, however, to separate platinum in this manner from the metallic oxides which are not precipitable from acid solutions by sulphuretted hydrogen gas. If a solution of platinum be made neutral or alcaline by soda, and an excess of bihydrosulphuret of ammonia be added, the precipitated sulphuret of platinum redissolves in the excess of the precipitant. By this process, therefore, platinum could be separated from those metals, whose sulphurets are insoluble in an excess of bihydrosulphuret of ammonia. It is, however, better, in all cases, to precipitate the platinum by muriate of ammonia or chloride of potassium; the other methods of separating it from metallic oxides in solution, are all inferior to this.

When the platinum presented for examination is in the metallic state, but combined with any of the metals which have been treated of in the foregoing sections, then the simplest method of separation would be that of treating the compound with nitric acid, by which all these metals, excepting the platinum, are oxidised and dissolved, while the platinum itself remains undissolved. It is, however, to be remarked, hereby, that platinum, when in combination with other metals, very often dissolves with these metals, in nitric acid. Platinum and silver, for example, cannot be separated by nitric acid, because the platinum partially dissolves with the silver in the nitric acid.

Analysis of Platinum Ore: Separation from Osmium, Iridium, Palladium, Rhodium, &c.—The separation of platinum from osmium, iridium, palladium, and rhodium, in combination with which, as well as with iron and copper, it occurs in the crude ore of platinum, is an operation accompanied by very great difficulties. BERZELIUS (POGGENDORFF'S Annalen, B. XIII. p. 553) has recently given us the following directions for the analysis of this ore, by which the difficulties which formerly attended the task are considerably lessened.

In the first place, the operator mechanically separates, from one another, those grains of the crude platinum which are distinguished by a different appearance. In the next place, all those are removed which the magnet is capable of attracting. Independently of the spangles of metallic iron which were first detected by OSANN (POGGENDORFF'S Annalen, B. X. p. 315), the platinum sand often contains metallic compounds of iron and platinum, not only capable of being attracted by the magnet, but even possessed of polarity. These grains have a different composition from those which are not magnetic. The operator separates them by the magnet, and estimates their relative proportion.

The ore is then treated with diluted muriatic acid. The object of this is, to free it from the coating of peroxide of iron, with which it is often bedecked, and to dissolve the metallic iron. The quantity of the iron separated from the ore, by this process, is thereupon estimated.

The ore must not be ignited, until it has previously been weighed; for, during the ignition, it commonly acquires a coating of peroxide of iron, and a consequent increase of weight. It is sufficient to dry it upon a hot sand-bath.

The plan of the analysis should be regulated according to the proportions and nature of the constituents of the ore submitted to examination: it remains the same, however, for all the ores of platinum which have hitherto been discovered, since both those from Asia and from America contain the same constituents, combined in rather different proportions. These constituents, arranged according to their respective proportions, are:—platinum, iron, iridium, copper, rhodium, palladium, and osmium. Iridium and osmium are found in the platinum ore in two different states; they are either actually alloyed with the other metals, or merely melted in the conglomerate, as little particles of osmium-iridium. In the first case, they dissolve with the platinum; in the last, they remain behind undissolved, under the form of shining white spangles, which are so soft and tender, that they form a streak when rubbed on the skin. If larger grains of osmium-iridium remain behind, it is a proof, that the operator has not properly picked them out. It is sometimes of importance to determine their relative proportion; this is best done by dissolving all the rest of the ore.

The operator must not employ too large a quantity of the ore for analysis: 5 grammes (about 77 Troy grains) is by far too much; BERZELIUS thinks 2 grammes (about 31 Troy grains) the most convenient quantity. Sometimes, however, when the object is, to determine with great accuracy the quantity of a constituent which occurs but in a very small relative proportion, a larger quantity of the ore must be dissolved. But, in that case, all the constituents, excepting the particular one of which it is question, are to be neglected.

BERZELIUS effectuates the solution of the weighed metal, by means of aqua regia, in a glass retort furnished with a receiver, which is kept constantly cold. The acid which distils over, during the solution, is yellow; this colour does not proceed merely from the presence of chlorine, but from the constituents of the solution, which, driven upwards in a fine cloud during the effervescence, are hindered from falling again into the retort by the disengaged deutoxide of nitrogen. This gas, therefore, carries them over into the solution in the receiver. Spangles of osmium-iridium are transferred in the same manner from the retort to the receiver. The acid is distilled till the liquid has the consistence of a sirup, and congeals on cooling. The saline mass is dissolved in the smallest possible quantity of water, and the solution is poured off with proper precaution. The acid, which was distilled over, is poured upon the undissolved residue in the retort, and again distilled. What remained undissolved after the first distillation, is, in general, dissolved in the second distillation. The liquid is, as before, distilled down to the consistence of a sirup. If the distilled liquor be not colourless, it must be returned into the retort, and redistilled. It commonly contains peroxide of osmium, of which a portion is lost by the redistillation; the quantity, however, is in general very small.

The colourless distilled liquor is diluted with water, and saturated, either with ammonia, or, if this should be thought too expensive, with hydrate of lime; the acid must, however, remain a little in excess. The object of this saturation is, to prevent the decomposition of the sulphuretted hydrogen gas, with which the solution is afterwards to be precipitated, by the predominant acid. This precipitation must be performed in a flask which can be closed by a stopple, and of such a size as to be nearly filled by the solution. As soon as the liquid contains an excess of sulphuretted hydrogen gas, the flask is closed, and placed aside to allow the precipitate to fall down. This sometimes requires one or two days. The clear liquor is then removed by a syphon, and the sulphuret of osmium is brought on a weighed filter, and is washed, dried, and weighed. According to theory, the resulting sulphuret of osmium should contain 60,6 per cent. of that metal; but it is not obtained free from excess of sulphur or of water, nor does it escape a partial oxidation while drying. According to some experiments made by BERZELIUS, with weighed quantities of this substance, it appears that the sulphuret of osmium obtained by the operation described above, contains from 50 to 52 per cent. of osmium. In general, however, the quantity of osmium is so small, that an error of some per cents. in the reckoning of the quantity of osmium contained in this preparation, is of no importance with respect to the analysis.

With respect, now, to the metallic solution, it happens sometimes, that, after dissolving the saline mass, the liquid smells of chlorine. This is owing to a decomposition of the chloride of palladium. The solution must be allowed to digest, until it no longer smells of chlorine. If the solution becomes troubled during the digestion, it is owing to the precipitation of oxide of palladium, which must be redissolved. The solution is filtered through a weighed filter, upon which the undissolved parts remain. These consist of grains of osmium-iridium, of the above mentioned spangles of the same alloy, and of grains of sand, &c., which could not be separated previous to the analysis. Sometimes, the operator finds, in addition to these substances, a black powder, which has the appearance of charcoal, and which is capable of passing through the filter during the washing of the other grains. This powder is peroxide of iridium. The chief cause of its production is the presence of too much nitric acid in the aqua regia. When the solvent is thus constituted, the iridium is oxidised by the nitric acid during the concentration of the saline solution, and chlorine is set at liberty. Thence arises the disadvantage, which is now difficult to be remedied, that the iridium cannot be separated from the osmium-iridium, since both are insoluble in all liquids. The operator must, therefore, from the beginning of the process, endeavour to prevent this effect, as it is afterwards so hard to apply a remedy.

The filtered solution is mixed with twice its bulk of alcohol of the specific gravity of 0,833, so that the mixture may contain about 60 per cent. of its volume of alcohol. A concentrated solution of chloride of potassium in water is now added as long as it throws down a precipitate. The precipitate consists of the double chlorides of potassium and platinum, and of potassium and iridium, contaminated with that of rhodium, and a little of that of palladium. The two latter substances are carried down by the former, much in the same manner that crystals in general enclose a portion of the mother-liquor in which they are formed. The precipitate has a fine lemon-yellow colour when it is free from iridium; but, when iridium is present, it possesses all the shades of red, from deep yellow to cinnabar colour. It is brought upon a filter, and washed with a mixture of spirits of wine, containing 60 per cent. of alcohol, with a small proportion of a concentrated solution of chloride of potassium. The washing is continued until the liquor which runs through the filter gives no precipitate with sulphuretted hydrogen gas.

The analytical operations are now divided into the examination of the washed precipitate *A*, and of the alcoholic solution *B*.

A. The washed double salt is dried and mingled, with the greatest degree of accuracy, with an equal weight of carbonate of soda. The filter, with that portion of the precipitate which cannot be separated from it, is burnt, and the ashes are mixed with a little carbonate of soda, and then added to the rest of the double salt. The whole is placed in a porcelain crucible, and very gently heated till the mass is black through and through. If this experiment were to be performed in a platinum crucible, the operator would expose himself to an accident which very easily occurs, that, namely, of having the crucible itself acted upon by the alcali, and an addition of platinum made to the chlorides; in consequence of which, the analysis would give an unexpected excess.

By this treatment, the double salts of the alcali are decomposed, and the platinum, whose oxygen passes away with the carbonic acid, is reduced; the rhodium and iridium meanwhile become oxidised, and remain in such a state as to permit of the separation of the platinum from them by solution. When, instead of following the process here recommended, the operator effects the precipitation of the double salts by muriate of ammonia, a method which has been generally practised, then the heating of the precipitate in a crucible not only reduces the platinum, but also the rhodium and the iridium; so that, upon subsequently treating the heated mass with aqua regia, all the three metals dissolve together.

The heated saline mass is washed with water, till the greater part of the salt is dissolved. Diluted muriatic acid is then added to the remainder, to extract the alcali combined with the oxides of iridium and rhodium. The mass is washed, dried, and ignited. The filter can be burnt, and an allowance be made for the weight of the ashes; but, it is to be observed, that the filter must be burnt by itself, lest the metallic oxides be reduced by the combustible gases disengaged from the paper. The mass is afterwards weighed.

When this has been done, the mass is mixed with five or six times its weight of bisulphate of potash, and the mixture is melted in a platinum crucible, in the manner which has been particularly described in speaking of the analysis of rhodium, at page 132. This operation is repeated several times, or as long as the flux acquires a colour.

The quantity of the rhodium can be determined by two methods. According to the first, the undissolved platinum is washed, ignited, and weighed, and the quantity of the dissolved peroxide of rhodium, which contains 71 per cent. of metal, is estimated from the loss of weight. According to the other method, the acid rhodium solution is mixed with carbonate of soda in excess; the mixture is evaporated to dryness, and the dry salt is ignited in a platinum crucible. Upon dissolving it again in water, the peroxide of rhodium then remains behind. It is brought on a filter, washed, ignited with the filter, and reduced by hydrogen gas. The resulting metal is weighed.—The best plan is, to employ both methods. The rhodium thus obtained, sometimes contains palladium. This is extracted by aqua regia. The solution of palladium is neutralised, and then precipitated by cyanuret of mercury. The weight of the palladium is abstracted from that of the rhodium.

After the separation of the rhodium, the metallic mass is next treated with exceedingly dilute aqua regia, through digestion with which, pure platinum is extracted. The solution appears very dark, in consequence of the presence of peroxide of iridium; but when it has become clear, it is found to possess a pure yellow colour. The clear liquor is decanted. Concentrated aqua regia, mixed with chloride of sodium, is now poured over the residue, and the mixture is evaporated to dryness. The chloride of sodium is added to prevent the formation of protochloride of platinum. In this more concentrated acid, a little iridium dissolves; but, if a concentrated acid were not employed, a notable quantity of platinum would remain with the iridium. Upon dissolving the dry mass, the peroxide of iridium remains behind. When it is washed with pure water, it almost always passes through the filter. To separate it from the solution of platinum, it is therefore necessary to wash it with a weak solution of chloride of sodium, and afterwards, for the sake of getting rid of the chloride of sodium, to wash it with a weak solution of muriate of ammonia, the last remains of which can be expelled by heat. The edulcorated substance is burnt with the filter, reduced by hydrogen gas, and weighed. The solution of soda salt which contains iridium is mixed with carbonate of soda, evaporated to dryness, and heated to redness. The product is, a mixture of platinum and peroxide of iridium, which being freed by washing from soluble salts, and then treated with aqua regia, leaves behind the peroxide of iridium. Caustic ammonia still precipitates from the solution a trace of brown oxide of iridium, which, however, is not quite free from platinum. The peroxide of iridium is reduced, and the metal is added to the quantity formerly obtained. To learn now the weight of the platinum, the operator must deduct the weight of the peroxide of rhodium, from the common weight of the platinum, the peroxide of rhodium, and the peroxide of iridium. He must then add to the weight of the iridium obtained, 12 per cent. of the weight of that metal, to produce the weight of the peroxide of iridium, which must also be deducted from the weight of the platinum. These two deductions having been made, the remainder gives the weight of the platinum. The reduction of the platinum from its solution, and the experimental determination of its weight, would only lengthen the operation, without increasing its accuracy.

B. Treatment of the spirituous solution.—This solution is poured into a flask provided with a ground glass stopper, and a current of sulphuretted hydrogen gas is passed through, till the solution is saturated. The flask is then closed, and allowed to stand for 12 hours in a warm place, at the end of which time, the precipitate will have subsided. Sometimes, the solution then appears red, in consequence of the presence either of rhodium or of sesquichloride of iridium. The solution is filtered, and the alcohol expelled by evaporation; an additional quantity of metallic sulphuret then precipitates, which is added to that formerly obtained. The precipitate consists of sulphuret of iridium, sulphuret of rhodium, sulphuret of palladium, and sulphuret of copper; while the filtered solution contains iron, a little iridium and rhodium, and a trace of manganese. During the evaporation of the alcohol, a deposit is formed in the vessel of a sort of greasy and disagreeable smelling sulphuret, which cannot be washed out. After the solution has been entirely washed away from this substance, it can be dissolved by pouring a little caustic ammonia into the capsule. The solution is now poured into a platinum crucible, and evaporated to dryness; the moist metallic sulphurets are then placed in the crucible, and roasted as long as sulphurous acid is produced. When the roasting is done, the operator pours concentrated muriatic acid over the mass. Basic sulphate of deutoxide of copper, and basic sulphate of peroxide of palladium, dissolve, forming a green or yellowish green solution; while the oxides of rhodium and iridium, with a small quantity of platinum, remain undissolved.

The solution in muriatic acid is mixed with chloride of potassium and nitric acid, and evaporated to dryness; a dark coloured saline mass is produced, which contains chloride of potassium, chloride of potassium and copper, and chloride of potassium and palladium. The first two of these salts, being soluble in alcohol of the specific gravity of 0,833, are extracted thereby; the palladium salt, which then remains behind alone, is brought upon a weighed filter, and washed with alcohol. It contains 28,84 per cent. of palladium. Instead of proceeding in the above manner, the operator can dissolve the saline mass in boiling hot water, and precipitate the palladium by cyanuret of mercury; but this method is more circumstantial. It deserves the preference, however, when too large a quantity of chloride of potassium has to be extracted by the alcohol.

This spirituous solution of the cupreous salt contains a trace of palladium, which, however, may be altogether neglected. The solution is evaporated to get rid of the alcohol, and the copper is precipitated either by caustic potash, or by adding sulphuric acid to the solution, and inserting metallic iron. If the operator wishes to separate the palladium from the copper, it must be dissolved in nitric acid; the solution must be neutralised, and the palladium precipitated by cyanuret of mercury. Upon this, there is sometimes formed an exceedingly slight precipitate of cupreous cyanuret of palladium; this is filtered, burnt with the filter, and weighed. Generally, however, the quantity is so small, that the weighing of it is impracticable.

Before BERZELIUS became acquainted with the chloride of potassium and palladium, he endeavoured to precipitate palladium by cyanuret of mercury; but he found that the precipitate produced thereby, in a solution of palladium which contained copper, was greenish; that upon drying, it became darker, and that it contained copper. He knew no other way of escaping from this difficulty than that of combining the metals with sulphuric acid, evaporating the solution to dryness, and gently igniting the salts for a short time; the object of this operation being to convert the palladium salt into the basic sulphate which is insoluble in water. But this is an operation which requires much precaution: if too strong a heat be applied, the copper salt itself decomposes; if too gentle a heat be applied, the palladium salt is decomposed imperfectly.

The roasted sulphurets which could not be dissolved by the muriatic acid, are fused with bisulphate of potash; the operation being repeated as often as the flux acquires a colour. This metallic mixture contains much more rhodium than the precipitated chloride of potassium and platinum obtained at the beginning of the analysis. The operator must proceed in the manner which has been described at the place referred to, even also, with respect to a remainder of palladium which it is usual to find again here. When the mass has been exhausted of rhodium by fusion with bisulphate of potash, it is treated with aqua regia, which dissolves a little platinum, and leaves peroxide of iridium.

The concentrated solution from which the sulphurets were precipitated, contains only iron, in the state of protochloride, a small quantity of iridium and rhodium, and a trace of manganese. It is mixed with a sufficient quantity of nitric acid, and boiled till the iron is fully peroxidised. The peroxide of iron is then precipitated by caustic ammonia, and the precipitate is washed, ignited, and weighed. This peroxide of iron contains iridium and rhodium, both in such a state of combination as to be dissolved with the peroxide of iron by muriatic acid. Upon making this solution, there remains, in consequence of the decomposition of a siliceous mineral, of which the platinum ore contains some grains, a small quantity of silicic acid undissolved: this, however, is commonly in too small a quantity to be taken into the reckoning of the analysis. The peroxide of iron is reduced by hydrogen gas, and the metal is dissolved in muriatic acid, which, towards the end, must be warmed. There then rests, undissolved, a small quantity of a black powder, which contains the metals in a condition not at present well understood. When this powder is exposed to an extremely gentle degree of heat, it decrepitates with a disengagement of light; when heated in a closed vessel, it gives much water, but produces no light. By ignition in the open air, it acquires the same degree of oxidation as the peroxide of iron. It is then weighed; its weight is deducted from that of the peroxide of iron; and from the weight of the latter, the quantity of iron is calculated.

The solution, which was precipitated by caustic ammonia, still contains iridium and rhodium. It is mixed with carbonate of soda, in sufficient quantity to decompose the ammoniacal salts, and is evaporated to dryness. The residue is gently ignited, and is then dissolved in water, boiling hot water, and precipitate the palladium by cyanuret of mercury; but this method is more circumstantial. It deserves the preference, however, when too large a quantity of chloride of potassium has to be extracted by the alcohol.

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The solution, which was precipitated by caustic ammonia, still contains iridium and rhodium. It is mixed with carbonate of soda, in sufficient quantity to decompose the ammoniacal salts, and is evaporated to dryness. The residue is gently ignited, and is then dissolved in water, upon which the metallic oxides remain undissolved. If too strong a heat be applied to the substance left by the evaporation, the solution afterwards obtained is yellow, and contains a little of the oxides in solution. This evil is avoided by employing only a moderate heat. The quantity of manganese contained in the metallic oxides is scarcely greater than is necessary to enable the operator to detect it. The manganese afforded by 30 grains of crude platinum, is a quantity that cannot be weighed. It can be extracted from the washed oxides by muriatic acid.

In order to avoid too great a number of little operations, BERZELIUS preserves the oxides of rhodium and iridium separated from the peroxide of iron and from the saline mass, and adds them to the remainder of the metallic sulphurets, which is to be treated with bisulphate of potash. The whole are thus analysed together.

XXX. GOLD.

Reduction by Protosulphate of Iron.—The quantitative estimation of gold in solution is effected by reducing it. The reduction can be effected by different processes, with equally good results. In general, a solution of protosulphate of iron is employed as the reducing agent. Gold is precipitated from its solutions thereby, in the state of a fine brown powder. If the solution contains merely perchloride of gold, or if it contains perchloride of gold in combination with muriatic acid, the gold is completely reduced: it is good, therefore, to acidulate the solution with muriatic acid. The reduced gold is filtered, very gently ignited, and weighed. The ignition can be performed in a platinum crucible.—If the gold solution contains nitric acid, which is frequently the case, the reduction of the gold must then be effected with more precaution: for, the aqua regia which the solution will contain, can easily redissolve a portion of the reduced gold. In this case, it is advisable, before the addition of the protosulphate of iron, to evaporate the gold solution nearly to dryness, or at any rate, until all the nitric acid has been expelled, and chlorine begins to be disengaged. Or, instead of this method, the operator may gradually add muriatic acid to the solution while it is being heated; the nitric acid is likewise decomposed by this process, which produces free chlorine. The solution is then diluted with water, and mixed with a sufficient quantity of protosulphate of iron. If the evaporation of the solution produce a deposition of gold, before the addition of the solution of protosulphate of iron, this does no harm: it is always the case, when the solution has been so far evaporated that chlorine begins to be disengaged, and protochloride of gold to be formed.—Gold can also be reduced from its solutions by the addition of a solution of protonitrate of mercury. This method of precipitating gold is, however, not so good as that described above. The solution must not, in this case, contain too much nitric acid. The resulting precipitate must be more strongly ignited than in the former case, in order that all the mercury may be expelled.

Reduction by Oxalic Acid.—In many cases, the operator can employ with advantage oxalic acid or oxalates in the reduction of gold. When a solution of pure oxalic acid is employed, the gold is slowly, indeed, but perfectly, reduced. The solution of gold must undergo a pretty long and warm digestion with the oxalic acid; about 48 hours is requisite. During the reduction of the gold, a disengagement of carbonic acid takes place, on which account, the operator must take care that nothing is lost by effervescence. The gold reduced by this process appears more in the form of fine yellow lamellæ, and not as powder, as it does when reduced by protosulphate of iron.—If the operator wishes to employ an oxalate, he can only take such as contain a base which can form, with the muriatic acid, a chloride that is soluble in water, and such, too, as, when nitric acid is present, can form with the nitric acid, no other than a soluble compound. The solution of gold must contain a quantity of free muriatic acid, sufficient to decompose the oxalate. If it contain too much nitric acid, then, in this case, as in the reduction of gold by protosulphate of iron, the aqua regia in the solution can redissolve a portion of the reduced gold: it is necessary, therefore, to expel the nitric acid, in the manner which has been described above.

Separation from the Oxides of most Metals.—Gold can also be precipitated in the metallic state by many other substances; those, however, which have been mentioned above, appear to act most effectually. In consequence of being so easily reducible from its solutions, gold can be readily separated from most of the metallic oxides which have hitherto been treated of; since but very few of these oxides can be precipitated from their solutions by the reagents which serve to reduce gold. In cases of separation, such as those alluded to, the reduction of gold by oxalic acid, or by an oxalate, is generally to be preferred to the reduction by protosulphate of iron; because, when the latter is employed, it becomes necessary, after the filtration of the solution from the reduced gold, to separate the iron before proceeding with the farther analysis of the solution.

When gold alone, unaccompanied by any other metal, is contained in a solution, the solution can be evaporated to dryness, and the dry mass be ignited, upon which reguline gold remains behind, providing that no other fixed substance formed part of the solution. The gold, however, is then spread over the whole surface of the vessel, and is much more difficult to be gathered together, than when it has been precipitated by a reducing substance.

Separation from Silver and base Metals by Cupellation and Nitric Acid.—When gold is to be separated from other metals, a variety of methods may be employed. If gold be combined with silver and base metals, the proportions of the constituents are determined by cupellation. The relative proportions of the constituents having been first determined approximately by a proof with the touchstone, the alloy is mingled with an accurately-weighed quantity of pure silver, which must amount to about 3¼ times the weight of the gold in the alloy. The proper quantity of lead is then added. After cupellation, there remains behind an alloy of gold and silver; having determined the weight of which, the operator can reckon the quantity of base metal from the loss of weight. The alloy of gold and silver is then hammered into thin leaves, which are rolled together, and exposed to ignition. A weighed quantity of this ignited alloy is treated with nitric acid; whereupon, a solution of the silver is obtained while the gold remains behind, preserving the form of the rolled leaves. Fresh quantities of nitric acid are added, until the solution last formed gives no precipitate with muriatic acid. The gold is then weighed, and the quantity of silver reckoned from the loss.—It is well known, that when silver is alloyed with a large quantity of gold, it cannot be separated from it by nitric acid. It is on this account, that, previous to the cupellation, such a quantity of silver is added to the alloy as is necessary to render it completely decomposable by nitric acid.

Separation from base Metals by Nitric Acid.—Since gold is not attacked by simple acids, it might, in general, be separated by diluted nitric acid from metals which are soluble in diluted nitric acid. The operator should not employ too strong an acid, nor should the nitric acid employed for this purpose be boiling, otherwise a portion of nitrous acid would be produced; the consequence of which might be the dissolving of an extremely slight trace of gold. It is, however, to be borne in mind, hereby, that there are many metals which, either when alone, or when combined with certain other metals, dissolve readily in nitric acid; but which, nevertheless, when alloyed with gold, and especially with a large proportion of gold, become altogether insoluble in nitric acid. It is, therefore better, in all cases, when an alloy of gold is to be quantitatively analysed, to dissolve it in aqua regia, to expel the excess of nitric acid from the solution by muriatic acid, and then to precipitate the gold, which, in this case, it is best to do by reduction with oxalic acid.

Separation from Silver by Aqua Regia.—Gold can very well be separated from silver, even when the gold is present in large proportion, by boiling the alloy in aqua regia: the gold is completely dissolved, while the silver, after dilution with a large quantity of water, remains perfectly undissolved. It is wholly converted, however, into chloride of silver, often preserving the external form of the compound submitted to analysis. From the solution filtered from the chloride of silver, the gold can be precipitated by protosulphate of iron.—Often, however, the resulting chloride of silver can, according to BOUSSINGAULT (POGGENDORFF'S Annalen, B. x. p. 315), contain a small kernel of gold, which, clothed by chloride of silver, has been protected from the action of the aqua regia. It is then better to employ cupellation; or to decant the solution, to dissolve the covering of chloride of silver by ammonia, and then to treat the kernel with a fresh quantity of aqua regia.

Precipitation by Sulphuretted Hydrogen Gas.—Gold can, moreover, be completely precipitated from an acid and diluted solution by sulphuretted hydrogen gas. It can, therefore, be thus separated from the substances which sulphuretted hydrogen gas is incapable of precipitating from acid solutions.—The precipitation must be effected in the cold, and the resulting black sulphuret of gold must be very speedily filtered; because, if the solution be allowed to repose, the sulphur of the sulphuret of gold becomes oxidised to sulphuric acid, and remains dissolved in the solution, while gold is set free. The sulphuret of gold is dried, and then ignited in a platinum crucible; the sulphur is volatilized, and metallic gold remains behind, and can be weighed.

Separation from Platinum.—As sulphuret of gold is dissolved by a great excess of bihydrosulphuret of ammonia, the separation of gold from platinum by that reagent is impracticable. The two metals can only be separated by concentrating their solution in aqua regia, mixing it with a solution of muriate of ammonia, or of chloride of potassium, and then adding alcohol. A precipitate is then formed, containing chloride of platinum with muriate of ammonia, or chloride of potassium. This must be washed with spirits of wine; after which, the quantity of platinum it contains, is to be estimated in the manner previously described. From the filtered solution, the gold is next precipitated, either by a solution of protosulphate of iron, or of oxalic acid.

XXXI. TIN.

Precipitation in the State of Peroxide of Tin.—The method by which tin is, in general, quantitatively estimated, is that of boiling it with nitric acid. This operation converts it into peroxide of tin, which is insoluble in that acid. When tin exists in solution, in the state of protoxide of tin, nitric acid is added, and the solution is concentrated by evaporation; the protoxide is thereby converted into peroxide, which is not only insoluble in nitric acid, but also in sulphuric acid. But if the solution contains a large quantity of muriatic acid, then a portion of the peroxide of tin can be dissolved; to prevent the ill effects of this acid, a sufficient quantity of nitric acid must be added to the solution, and the whole must be evaporated till the muriatic acid is either destroyed or expelled. The resulting insoluble peroxide of tin is thereupon filtered, ignited, and weighed. The operation is conducted in a similar manner, when the solution contains peroxide of tin. It is then likewise boiled with nitric acid till the peroxide of tin is precipitated. Even when the solution contains that peculiar sort of peroxide of tin which is obtained from the perchloride of tin, and which is partially soluble in cold nitric acid, still, the operator obtains, by boiling the solution with nitric acid, that other modification of the peroxide of tin which is insoluble in nitric acid.

Precipitation by Sulphuretted Hydrogen Gas.—Tin, whether it be contained in solution as protoxide or peroxide, can be completely precipitated by sulphuretted hydrogen gas: the solution must be sufficiently diluted with water, but it may be either neutral or acid. From solutions of protoxide, the sulphuret of tin precipitated by sulphuretted hydrogen gas is brown; from solutions of peroxide, the sulphuret of tin precipitated is yellow. The yellow sulphuret of tin, which corresponds with the peroxide, subsides much more slowly than that which corresponds with the protoxide. When peroxide of tin is precipitated from solution by sulphuretted hydrogen gas, and the solution has been completely saturated with the precipitant, then a little sulphuret of tin is dissolved by the free sulphuretted hydrogen gas. This portion of sulphuret of tin is, however, again perfectly precipitated, when the solution is digested in a very gentle heat, until it no longer smells of sulphuretted hydrogen. The resulting sulphuret of tin might be filtered on a weighed filter, and be thereon dried and weighed. The quantity of peroxide or protoxide, according as one or the other of these was contained in the solution, could then be calculated from the weight of the sulphuret of tin. But when it is not known which of the oxides of tin was present in the solution, or when the solution held a mixture of both oxides, then, this mode of proceeding cannot be adopted. The best method of determining how much tin is contained in the resulting sulphuret of tin, is the following: The edulcorated sulphuret is brought with the filter, while still wet, into a capacious glass, or into a flask with a wide mouth, which can, however, be closed with a glass stopper. The operator then, gradually, and with proper precaution, pours fuming nitric acid over the sulphuret, during which, he must take particular care that nothing is lost by the spirting produced by the violent action that takes place. The tin is thus converted into insoluble peroxide of tin; the sulphur, into sulphuric acid. The peroxide of tin can now be filtered, ignited, and weighed; it is better, however, to transfer the whole into a platinum vessel, and to evaporate the nitric acid first by a gentle heat, and afterwards the sulphuric acid by a stronger heat. The peroxide of tin remaining behind is then exposed to ignition in a platinum crucible, upon which the sulphuric acid is entirely expelled, and pure peroxide of tin remains behind; when this has been weighed, the quantity of tin can be reckoned. Although this method is more circumstantial, it is still far preferable to that in which the precipitated sulphuret of tin is converted into peroxide of tin by strong ignition, with access of air. The perfect conversion of the one into the other, is effected in this manner, if the quantity of sulphuret of tin be at all considerable, very difficultly, and with extreme slowness: when, however, the quantity of sulphuret of tin is very small, this method can be employed with much advantage.

Separation from most other Metals.—The separation of tin from other metals is not attended with much difficulty. If metallic tin, combined with other metals, be presented for analysis, the alloy is boiled with nitric acid. All the metals which have hitherto been treated of, those termed noble metals, for example, platinum, gold, &c. being excepted, are oxidised by nitric acid, and all the oxides so produced, the peroxide of tin alone excepted, are dissolved by nitric acid; upon filtering the nitric acid solution, therefore, the tin and the other metals are separated. The peroxide of tin is weighed, and the quantity of metallic tin is calculated.—When, however, platinum and gold are contained in the alloy, aqua regia must be employed to effect the separation, instead of nitric acid. Both metals are thereby dissolved, and the peroxide of tin remains in totality behind, if care be taken, previous to the filtration of the peroxide of tin, to destroy as completely as possible the free muriatic acid in the solution, by the addition of nitric acid. A better method of separating platinum and gold from tin, would be that of treating the alloy with gaseous chlorine, in an apparatus, such as has been described at page 77. Perchloride of tin would be thereby produced, which, after volatilization, would be dissolved in the water of the flask. The gold and platinum would remain behind, combined with more or less chlorine, according as a stronger or weaker heat had been applied during the experiment.

Separation from the Oxides of Uranium, Nickel, Cobalt, Zinc, Iron, and Manganese; and from the Earths and Alcalies.—The oxides of tin can also be separated, by sulphuretted hydrogen gas, from all the substances which that reagent is incapable of precipitating from acid solutions. They can, consequently, be thus separated from the oxides of uranium, nickel, cobalt, zinc, iron, and manganese; and from the earths and alcalies.

Separation from the Oxides of Cadmium, Lead, Bismuth, Copper, Silver, and Mercury.—To separate the oxides of tin from those of cadmium, lead, bismuth, copper, silver, and mercury, the whole of which are precipitable from acid solutions by sulphuretted hydrogen gas, the best way to proceed is, to supersaturate the concentrated solution with ammonia, and to precipitate it by an excess of bihydrosulphuret of ammonia. The sulphuret of tin is thereupon redissolved, while the other sulphurets remain undissolved. The sulphuret of tin at the maximum of sulphur, which corresponds with the peroxide of tin, is much easier dissolved by an excess of bihydrosulphuret of ammonia than the sulphuret which corresponds with the protoxide of tin. The latter would probably be insoluble, if the bihydrosulphuret of ammonia could be obtained perfectly free from excess of sulphur. The mixture of the ammoniacal metallic solution with the bihydrosulphuret of ammonia must be digested at a very gentle heat, in a matrass closed, but not completely air-tight, by a cork; the metallic sulphurets which are insoluble in bihydrosulphuret of ammonia then subside better, and the solution of the sulphuret of tin more easily follows. If the solution contain protoxide of tin, then the bihydrosulphuret of ammonia which is employed, must be mixed with a little powdered sulphur; this has the effect of producing the highest sulphuret of tin, which is easily soluble in bihydrosulphuret of ammonia. The undissolved sulphurets are filtered, and washed with water mingled with bihydrosulphuret of ammonia. They are then examined, according to methods which have been given in the preceding sections, with a view to the quantitative estimation of the metals which they contain. To the solution, filtered from the sulphurets and diluted, muriatic acid is cautiously added, until the solution is acid; whereupon, sulphuretted hydrogen gas is set free, and sulphuret of tin precipitates. The solution is digested, in a gentle heat, until it no longer smells of sulphuretted hydrogen. The sulphuret of tin is then filtered, and converted into peroxide of tin, by the process described above.

Separation of Protoxide of Tin from Peroxide of Tin.—If a solution contain both the protoxide and the peroxide of tin, or the protochloride and the perchloride, and the quantity of each is to be determined, the best way to proceed is as follows: The tin solution is gradually poured into a solution of perchloride of mercury, whereupon, the protoxide or protochloride of tin converts a portion of the perchloride of mercury into protochloride of mercury, which precipitates in the form of insoluble scaly crystals. It is filtered upon a weighed filter, washed, dried at a very gentle heat, and weighed. From the weight of this protochloride of mercury it is easy to calculate how much protoxide or protochloride of tin was contained in the solution from which it was precipitated; for the quantity of chlorine contained in the protochloride of mercury is the same as the quantity of chlorine contained in the protochloride of tin by which it was precipitated, or, on the other hand, the quantity of chlorine in the protochloride of mercury is equivalent to the quantity of oxygen in the protoxide of tin which acted as a precipitant. Knowing this, it is easy to find the quantity of protoxide or protochloride of tin. With another portion of the solution, the quantity of tin is determined by one of the methods described above; best of all, perhaps, by means of sulphuretted hydrogen gas. From the quantity of tin, it is then easy to reckon that of the peroxide or perchloride of tin.—In the precipitation of the protochloride of mercury, the precaution is to be observed, of dropping the solution of tin into the solution of perchloride of mercury, and, secondly, of having an excess of perchloride of mercury in the solution; otherwise, the protochloride of mercury might, in both cases, be reduced to metallic mercury. The whole must, besides, be warmed, and the resulting protochloride of mercury be allowed to repose some time before filtration.

Analysis of Native Peroxide of Tin.—Peroxide of tin occurs in nature, combined with but few foreign substances, and yet in such a state of compactness as to be insoluble in acids. Factitious peroxide of tin also acquires the property of insolubility in acids, by being heated to redness. If the chemist desires to determine quantitatively the small admixture of foreign substances in the native peroxide, it is necessary to reduce the mineral to a very fine powder by levigation, to mix it with three or four times its quantity of carbonate of potash or carbonate of soda, and therewith to ignite it. Carbonic acid gas is then disengaged by the carbonate of potash, so that the heat must be applied very gradually. The same measures of precaution are to be observed in this case, as in the fusing of silicic acid or silicates with carbonated alcalies; it is unnecessary, however, to describe them circumstantially here, since they will be properly explained farther on, under the article Silicium.—After fusion with the alcali, the peroxide of tin is soluble in acids. The operator can then estimate, not only the quantity of the peroxide of tin, but of the foreign substances which were combined with it, and which now form part of the solution.

XXXII. TITANIUM.

Precipitation of Titanic Acid by Ammonia.—Titanium is best precipitated from solutions in which it exists as titanic acid, by ammonia. The precipitate is bulky, and similar to that afforded by alumina. A great excess of ammonia must be avoided, otherwise an extremely small quantity of titanic acid may remain in solution. It is therefore advisable, after effecting the precipitation by ammonia, to allow the whole to remain in a warm place, until the greater part of the excess of ammonia has volatilized. The bulky precipitate of titanic acid shrinks very considerably during the drying: when dry, it is ignited, and weighed. It acquires a strong lustre from the ignition. The weighing must be performed in a well-closed platinum crucible, and as soon as the crucible is cool enough to be handled; otherwise, the titanic acid increases very considerably in weight, by the attraction of moisture.

Precipitation of Titanic Acid by boiling the Solution.—Chemists have often adopted the method of precipitating titanic acid from its acid solutions by a continued boiling of the liquid; the titanic acid is thereby rendered insoluble in the acid by which it was dissolved, and is obtained in the form of a heavy precipitate. But even when the boiling has been continued for a long time, there always remains a portion of titanic acid in solution; and this portion can only be obtained by evaporating the solution to dryness. When the titanic acid, precipitated by boiling, is filtered, the solution passes through the filter as clear as it need do, as long as it is acid; but if the attempt be made, to wash the titanic acid with pure water, the liquid passes through the filter like milk, and, finally, if the washing with water be continued, carries all the titanic acid away, and leaves nothing on the filter. The employment of strong filtering paper does not prevent this effect. It can only be prevented by edulcorating the precipitate with a mixture of water and acid, though even in that case, a portion of titanic acid is still dissolved.—It is only when titanic acid is dissolved in sulphuric acid, that, according to BERZELIUS, upon diluting the solution with a large quantity of water and then boiling it, the titanic acid can be fully precipitated.

For the reasons above mentioned, the titanic acid cannot be separated from other substances, by boiling the acid solution, and filtering the precipitated titanic acid from the solution of the dissolved substances. Even if the titanic acid were to be fully precipitated, which, however, is never the case, yet then, so many difficulties would arise from the impossibility of properly washing the precipitate, that, even on that account, this method of separation could not be employed. It has been proposed to overcome the difficulties of washing the titanic acid, precipitated by boiling, by employing a solution of some salt of ammonia. This was to prevent the passing of the titanic acid through the filter with the water, and the consequent formation of a milky solution. But unfortunately, the ammoniacal salt either does not prevent the effect, or it makes the titanic acid stop the pores of the paper so completely that the wash-water can no longer pass through. If a little ammonia is added, then indeed the liquid runs clear from the filter; but if the substance, which is to be separated from the titanic acid, be precipitable by ammonia, the object of the washing is, of course, quite lost.—More recently, the following method has been proposed: When the precipitation of the titanic acid has been effected by boiling, the acid solution is evaporated, either quite, or nearly, to dryness; the evaporated mass is then treated, either with pure or acidulated water. But all these methods are too imperfect to give results even approximating to accuracy.

To separate titanic acid quantitatively from foreign substances, the operator must therefore proceed after other methods. Analyses of this kind are often accompanied by difficulties so great, that chemists are still far from being able to separate titanic acid with accuracy from all other substances.

Separation from the Oxides of Tin, Mercury, Silver, Copper, Bismuth, Lead, and Cadmium.—As titanic acid is not precipitable from acid solutions by sulphuretted hydrogen gas, it can be separated from all the metallic oxides which sulphuretted hydrogen gas precipitates from acid solutions.

Separation from the Oxides of Cobalt, Zinc, Manganese, &c.—The metals which are precipitated in the state of sulphurets, from neutral or alcaline solutions by bihydrosulphuret of ammonia, can be perfectly separated from titanic acid by the following process: The operator adds to the solution, which in general can only be acid, a solution of tartaric acid, which renders, not only the titanic acid, but also nearly all the oxides with which it can exist in solution, incapable of precipitation by ammonia. The solution is then supersaturated with ammonia, upon which no precipitate is formed, if the proper quantity of tartaric acid has been added. To this ammoniacal solution, bihydrosulphuret of ammonia is now added, whereupon, all the metallic oxides are precipitated as sulphurets, while the titanic acid remains unacted upon. The precipitate is filtered, and washed with water to which bihydrosulphuret of ammonia has been added. To determine from these sulphurets, the quantity of oxides which existed in the solution, the precipitate must be treated in the manner which has been previously described.—It is now more difficult to determine the quantity of titanic acid existing in the solution filtered from the metallic sulphurets. If no fixed constituents be contained in the solution besides the titanic acid, it is then unnecessary to destroy the excess of bihydrosulphuret of ammonia by the addition of an acid; but the solution is evaporated to dryness, and the dry mass is ignited, with the access of air, in a counterpoised platinum crucible, or in a small counterpoised platinum capsule, until all the volatile constituents have been expelled, and the charcoal of the tartaric acid has been completely consumed. The tartaric acid alone then remains behind, and can be weighed. It is somewhat difficult, however, fully to burn away the charcoal in a platinum crucible over the spirit lamp with double current of air; but this is effected both easily and completely, when the counterpoised platinum crucible is placed in the muffle of a small heated assay furnace. If the tartaric acid employed contained lime, which is almost invariably the case with the tartaric acid obtained from chemical works, then the whole quantity of lime remains behind with the titanic acid, the weight of which will be thereby much increased. In this case, the resulting titanic acid must be mixed in a platinum crucible, with from three to four times its weight of carbonate of potash or of soda, and be fused therewith. The fused mass is then to be subjected to the action of diluted muriatic acid, in which it completely dissolves if the application of heat is avoided. The solution is diluted with water, and the titanic acid is precipitated by ammonia.

Separation from the Oxides of Iron.—The above method is particularly adapted to the separation of titanic acid from the oxides of iron, with which it forms compounds that occur in nature. But as the titanic acid is commonly combined both with peroxide and protoxide of iron, the analysis must be performed with two different portions of the compound. The two weighed quantities, previously levigated and dried, are placed in glasses which can be closed air-tight with glass stopples, and are subjected therein to the action of strong muriatic acid. The compounds then dissolve completely, with the exception of a very small remainder, consisting of impure titanic acid. To one of the solutions so produced, a solution of chloride of sodium and gold is added, for the purpose of ascertaining, in the manner described at page 71, the quantity of protoxide of iron contained in the substance, from the quantity of gold which it precipitates. The precipitated and weighed gold is thereafter dissolved in aqua regia, and the impure titanic acid is left behind in an undissolved state. This is ignited and weighed, and its weight is deducted from that of the weighed portion of the compound, as an unessential ingredient. To the other solution, liquid sulphuretted hydrogen is added, with a view to determine, by the method described at page 69, the quantity of peroxide of iron which is present. The precipitated sulphur is weighed upon a weighed filter, and then is burnt, upon which the small portion of impure titanic acid remains behind, and can be weighed. Its weight is deducted, both from the weight of the sulphur and that of the portion of the compound employed for analysis. The solution filtered from the sulphur is mixed with tartaric acid, and supersaturated with ammonia; the iron is then precipitated as sulphuret of iron, by bihydrosulphuret of ammonia. The sulphuret of iron is afterwards converted into peroxide of iron, by the process described at page 54; and from the weight of the peroxide of iron, the quantity of metallic iron is calculated. The quantity of iron found thus, must agree with that which is found, by calculation, to exist in the peroxide and protoxide of the compound submitted to analysis. The titanic acid existing in the liquid filtered from the sulphuret of iron can afterwards be estimated.

Separation from Zirconia.—The greatest difficulties attend the separation of titanic acid from substances which can be precipitated as sulphurets, neither by sulphuretted hydrogen gas nor by bihydrosulphuret of ammonia, and which, on the contrary, are fully precipitated, like titanic acid itself, by ammonia. Titanic acid occurs in nature combined with many such substances, for example, with zirconia; yet no method has yet been discovered of accurately separating these substances; the many properties which they possess in common, rendering their separation extremely difficult. Titanic acid, too, when in combination with zirconia, possesses many properties which, in other circumstances, are wanting. When, for example, both titanic acid and zirconia are in a sulphuric acid solution, and the solution is boiled, then, according to BERZELIUS (POGGENDORFF'S Annalen, B. VI. p. 232), a muddiness is occasioned, and a portion of titanic acid is deposited; yet the greater part of the latter remains dissolved in the solution. When, however, titanic acid alone is contained in a sulphuric acid solution, it is completely precipitated by boiling, while zirconia, under the same circumstances, is not affected by boiling. Titanic acid is also precipitated from its solution by prussiate of potash; zirconia, on the other hand, is not precipitated by that reagent. But if both these substances are in a solution together, then prussiate of potash produces no precipitate.

Separation from the Oxides of Cerium and Yttrium.—The separation of titanic acid from the oxides of cerium and yttria, with which it occurs in many native compounds, is likewise difficult to be effected. The only method by means of which either of the above oxides can be separated, is that of dissolving the compound in sulphuric acid, and boiling the solution to precipitate the titanic acid. The oxides of cerium and the yttria are afterwards separated from the filtered solution, in the manner which has been described at page 40.—The separation cannot be effected by carbonate of ammonia, because titanic acid is not quite insoluble in carbonate of ammonia.

Separation from Magnesia.—Titanic acid can be separated from magnesia by ammonia. Before effecting the precipitation, it is necessary to add such a quantity of muriate of ammonia to the solution, as is sufficient to render the magnesia incapable of precipitation by ammonia.

Separation from Lime.—From lime, with which titanic acid is found in nature in the mineral called sphene, the titanic acid can be very well separated by ammonia. The operator must take care, during the filtration, to protect the precipitated titanic acid as much as possible from the action of atmospheric air, in order that no contamination with carbonate of lime may take place.

Separation from Barytes, Strontian, and the Fixed Alcalies.—Titanic acid is separated from barytes and strontian by sulphuric acid; from the fixed alcalies, by ammonia.

Methods of forming Solutions of the Titanates.—When titanic acid is combined with fixed bases, the compounds are soluble in muriatic acid, even after they have been ignited. This is the case, for example, with the native compounds of titanic acid, with protoxide of iron, peroxide of iron, and lime. The factitious compounds of titanic acid with potash and soda, likewise dissolve in muriatic acid, after having been ignited; provided there be no deficiency of alcali, nor excess of titanic acid. When any native compounds of titanic acid are to be dissolved in muriatic acid, they must, in the first place, be finely levigated, and again dried: the proper quantity must then be weighed out, and submitted to the action of strong muriatic acid, in a glass which can be closed air-tight with a glass stopple. They then dissolve, slowly indeed, but completely. In general, there remains undissolved a small quantity of impure titanic acid, the weight of which is determined. A very moderate heat has the effect of making the solution of the compound of titanic acid, in the muriatic acid, proceed more rapidly; but if heat be applied for that purpose, it must be applied with the utmost degree of precaution, because if the heat should rise in the slightest degree above what is necessary to effect the solution of the titanate, it would immediately throw down the titanic acid as an insoluble precipitate.

Method of dissolving Titanic Acid.—When titanic acid has been ignited, it is just as completely insoluble in muriatic acid, as the titanic acid which occurs in nature, constituting the mineral called rutile. If the titanic acid should not be quite pure, and the operator is desirous of accurately determining the quantity of the foreign admixtures, the titanic acid must be levigated, and then mixed in a large platinum crucible, with from three to four times its weight of carbonate of potash or carbonate of soda; and the mixture must be exposed to ignition. The heat must be cautiously and gradually applied, since, were the carbonic acid to be too suddenly liberated from the carbonate of potash, by the immediate application of a powerful heat, a loss from effervescence could be occasioned. In the fusion of titanic acid with the carbonates of alcalies, the same precautionary measures are to be employed as in the fusion of silicic acid, or the silicates, with the carbonates of alcalies. As the latter operation will be circumstantially described in a subsequent section, it is unnecessary to speak of it at length here.—The resulting titanate of alcali is completely soluble in muriatic acid. In the solution which is formed, the titanic acid, and the substances which were combined with it, are now to be estimated.

XXXIII. ANTIMONY.

Precipitation by Sulphuretted Hydrogen Gas.—Antimony can be fully precipitated from its solutions, whether it be present in them as oxide of antimony, or as antimonious or antimonic acid, only by acidulating and diluting those solutions, and then subjecting them to the action of sulphuretted hydrogen gas. The result afforded by this process, is a precipitate of orange-red coloured sulphuret of antimony. When it is oxide of antimony that is in the solution, the precipitate produced has a more brick-red colour; whereas, the presence of antimonious or antimonic acid in the solution, makes the colour of the precipitate tend more to yellow: at the same time, however, it must be observed, that the difference in the colour of the precipitates thrown down by sulphuretted hydrogen gas from solutions of antimony, depends also upon the more or less diluted state of the solutions. As the most concentrated acid solutions of antimony are decomposed upon being diluted with water, and then let fall a white precipitate, it is proper, before diluting them with water, to add a suitable quantity of pure tartaric acid. When this addition has been made, any solution of antimony whatever may be diluted with as much water as the operator chooses to employ, without being rendered in the least degree milky. It is advisable, to observe the following rule as much as possible: It is always better to lead sulphuretted hydrogen gas through a clear than through a milky solution; since, when proper care is not taken, it often happens that a portion of the precipitate, especially when it is heavy, escapes the action of the sulphuretted hydrogen gas.

When the current of sulphuretted hydrogen gas has passed so long through the solution of antimony, that the latter is quite saturated therewith and smells strongly of sulphuretted hydrogen, then the solution is exposed to an extremely gentle heat, until the smell of sulphuretted hydrogen gas is no longer perceptible. This precaution is absolutely necessary, because traces of sulphuret of antimony, by no means inconsiderable, remain dissolved in a solution saturated with sulphuretted hydrogen gas; and this portion of sulphuret of antimony does not completely precipitate, until the solution is entirely deprived of free sulphuretted hydrogen. The sulphuret of antimony is thereupon filtered upon an accurately weighed filter; it is washed with pure water, and dried by exposure to an extremely gentle heat, until it no longer loses weight. It is then weighed.

It is in but few cases advisable, to determine the quantity of antimony from the weight of the sulphuret of antimony. This can be done in those cases only, in which the operator knows with certainty that the solution of antimony contained merely the *oxide* of antimony. And this can be the case, only when the oxide of antimony, or the compounds of sulphur and antimony, have been dissolved in concentrated muriatic acid. Even then, however, the sulphuret of antimony obtained contains a small portion of free sulphur, the precipitation of which takes place in consequence of the decomposition of the excess of sulphuretted hydrogen gas, after the precipitation of the antimony. In solutions made with aqua regia, the operator has always mixtures of several of the oxides of antimony; and whenever tartaric acid is present, the sulphuret of antimony, which is then precipitated from solutions of antimonious acid, is not equivalent to that acid, but to antimonic acid. If, however, the operator determines to reckon how much antimony or oxide of antimony, is equivalent to the weight of the dried sulphuret of antimony, obtained by precipitation from a solution of oxide of antimony, he must, at any rate, never neglect to dissolve a small quantity of the sulphuret in concentrated muriatic acid. If it dissolve entirely, under disengagement of sulphuretted hydrogen gas, he may then be assured that the sulphuret of antimony he has obtained, is equivalent to the oxide of antimony; if, however, upon making this solution, sulphur remains undissolved, the operator is then reduced to the necessity of examining how much antimony is contained in a weighed quantity of the given sulphuret. The result afforded by that examination, furnishes him with the means of estimating the whole quantity of antimony. This examination must always be entered upon, when the antimony contained in the solution, from which it was precipitated by sulphuretted hydrogen gas, was in a high state of oxidation.

Analysis of the Sulphurets of Antimony: I. *By Oxidation with Nitric Acid.*—The examination of the sulphuret of antimony, undertaken to determine the quantity of antimony it may contain, is capable of being carried on in two different ways. One of the methods is as follows: The dried sulphuret of antimony is accurately weighed with the filter. The greater part of it, that is to say, as much as can be separated from the filter without rubbing the paper, is then shaken into a matrass; and the filter with that portion of the sulphuret of antimony that still hangs upon it, is again weighed: the operator thus ascertains with exactness how much of the sulphuret of antimony is employed in the experiment. Fuming nitric acid is now dropped into the matrass. This is done very gradually, and with the utmost precaution. The too sudden or too rapid addition of the acid would occasion, by the violence of its action, a spirting about, which is carefully to be guarded against. Afterwards, more nitric acid is added, and as much muriatic acid is poured in, as is sufficient to cause the entire solution of the antimony. If, instead of the fuming nitric acid, the operator were to employ weaker nitric acid, or aqua regia (unless the latter were extremely concentrated), then it would be possible for a slight trace of sulphuretted hydrogen gas to be disengaged from the very finely-divided sulphuret of antimony, an effect which is carefully to be shunned. Still, it *is* possible to oxidise the sulphuret of antimony by means of such nitric acid as is too weak to fume; but it is then necessary to heat the acid nearly to boiling; after some time, muriatic acid is also added, for the purpose of dissolving the oxidised antimony. The aqua regia may be allowed to digest with the sulphuret of antimony, either till nothing remains undissolved, except a small quantity of yellow sulphur, or even till this remainder of sulphur is dissolved. In general, when concentrated and fuming nitric acid is employed, the whole of the sulphur is fully oxidised; or if any sulphur remains undissolved, the quantity of it is extremely small. The solution is mixed with a sufficient quantity of tartaric acid, and diluted with water; the sulphur which may remain behind is thereupon filtered upon a very small weighed filter. It is carefully dried by the application of an exceedingly gentle degree of heat, and is then weighed. To the filtered liquid, a solution of chloride of barium is added, as long as it produces a precipitate; the whole is then moderately warmed, that the precipitated sulphate of barytes may properly subside. It is then filtered, washed, ignited, and weighed. The quantity of sulphur is calculated from the weight of the sulphate of barytes. When, in consequence of treating the sulphuret of antimony by aqua regia, a portion of undissolved sulphur is separated, the weight of this portion is added to that which calculation proves to exist in the sulphate of barytes. The weight of the sulphur is then deducted from that of the portion of sulphuret of antimony employed in the experiment; the remainder shows how much antimony was present.

Analysis of the Sulphurets of Antimony: II. *By Reduction with Hydrogen Gas.*—The other method of determining the quantity of antimony, in the sulphuret of antimony, consists in heating a weighed quantity of the sulphuret in an atmosphere of hydrogen gas. Decomposition is effected; and metallic antimony is obtained, and can be weighed. The apparatus employed for this purpose, is the same as that which is made use of in the reduction of oxide of cobalt. It has already been described and represented at page 83. When the sulphuret of mercury obtained by precipitation has been dried and weighed upon a weighed filter, the greater part of it is taken from the filter, and placed in an accurately weighed apparatus, consisting of a glass bulb, having a glass tube soldered on each side of it. The sulphuret is inserted, with care, in the bulb, and the interior of the glass tube on each side of the bulb is cleansed with the plume of a feather. The apparatus is now again weighed. The difference of the two weighings shows how much of the sulphuret is employed in the experiment. Dry hydrogen gas is now passed through the apparatus; and when the latter is quite filled with the gas, the bulb, which contains the sulphuret of antimony, is gradually heated. If the sulphuret of antimony is so constituted as to be equivalent to the oxide of antimony, then all the sulphur is converted into sulphuretted hydrogen gas, and antimony alone remains behind; but, if it is a higher sulphuret of antimony, or if it is a mixture of several sulphurets, then metallic antimony remains, indeed, behind, as in the preceding case; sulphuretted hydrogen gas is also disengaged, while free sulphur forms an additional product. The sublimate of sulphur appears first, and then the formation of sulphuretted hydrogen gas proceeds. The sulphur, at first, deposits itself on the upper part of the bulb; but the continued heat and the current of hydrogen gas drive it thence towards that end of the glass tube which is most distant from the flask in which the hydrogen gas is generated. As fast as the sulphur sublimes, it is expelled from the tube by the flame of a small spirit lamp. When sulphur ceases to be sublimed, and sulphuretted hydrogen gas to be disengaged, the whole is allowed to cool; the current of hydrogen gas being continually kept up while the apparatus is cooling. When cold, the apparatus is taken to pieces, and the bulb, with its tubes, and the antimony within it, are weighed. The loss of weight indicates the quantity of sulphur; what remains behind, is metallic antimony.

The result afforded by this method is not quite so accurate as that afforded by the first method. It is altogether impossible to prevent the sublimation of a small portion of antimony. This is deposited, partly on the upper surface of the bulb, and partly in the tube. The latter is more particularly the case, when a very strong heat is applied during the operation. A portion of the antimony, which, however, is extraordinarily small, is moreover actually carried out of the tube by the hydrogen gas. It is in consequence of this, that, towards the end of the operation, the disengaged gas burns with a flame, which is accompanied by a scarcely-observable smoke of antimony, and that the opening of the tube, where the gas burns, exhibits an exceedingly slight deposite of oxide of antimony. Hence it is, too, that the operator obtains in most analyses, somewhat less antimony and more sulphur than he properly should obtain; for, as the quantity of sulphur is estimated from the loss of weight, it follows, of course, that every additional loss comes to be reckoned as sulphur. But the quantity of antimony which can be lost in this manner, amounts, at the highest, to but a half per cent., provided the operation be performed with proper care.—The more gradually the sulphuret of antimony is heated, the less antimony is volatilized. At the end of the operation, however, a strong heat must be given for a short time. The reduced antimony does not run together into a single lump, but forms a number of small metallic grains. When the sulphuret of antimony has been gently heated for a very long time, while exposed to the current of hydrogen gas, the reduced antimony exhibits crystal facets, the glance of which makes the antimony appear of a blacker colour than that reduced by a stronger heat.

Analysis of the Sulphurets of Antimony: III. *By Heat.* —All the higher sulphurets of antimony can be converted into the lowest sulphuret, by being heated out of contact with atmospheric air. The quantity of antimony can then be reckoned from the weight of the resulting sulphuret. This method, however, does not give an accurate result; partly, because the lowest sulphuret of antimony is not quite incapable of volatilization; partly, because the atmospheric air in the little retort or matrass in which the experiment must be performed, produces a small quantity of oxide of antimony. This oxide of antimony combines with the sublimed sulphur in the neck of the retort, and forms a compound of sulphuret and oxide of antimony.

Separation from other Metals by Nitric Acid.—With respect to the separation of antimony from other metals, a method often employed, is, that of treating the reguline compounds of antimony by nitric acid, which oxidises the antimony, and renders it insoluble. The result afforded by this method is by no means so accurate with antimony, as the result afforded when tin is thus separated by nitric acid. The oxide of antimony is not so insoluble in nitric acid as the oxide of tin; when, therefore, the solution is filtered from the oxide of antimony, it is found to contain not only the other metallic oxides in solution, but traces also, by no means inconsiderable, of oxide of antimony.

Separation from the Alcalies and Earths.—The best method of separating antimony from other substances, is to convert it, by sulphuretted hydrogen gas, into sulphuret of antimony. If it is combined with such oxides as cannot be precipitated from acid solutions by sulphuretted hydrogen gas, the gas is then passed at once through the acid solution, and the antimony is thereby precipitated. When antimony is separated in this manner from the earths and alcalies, it is advisable to avoid the addition of tartaric acid to the solution; for, when tartaric acid is added to solutions of earths and metallic oxides, it has generally the effect, if present in a certain proportion, of hindering the precipitation of these substances by alcalies. In a solution filtered from the sulphuret of antimony, and containing tartaric acid, barytes alone can, in consequence of its perfect precipitation by sulphuric acid, be properly estimated. Alumina and magnesia, on the contrary, are totally incapable of being precipitated by alcalies. When, therefore, the oxides of antimony are to be separated from the earths and alcalies, the best way to proceed, is, either to add as much diluted muriatic acid as is sufficient to render the solution clear, or to permit the sulphuretted hydrogen gas to pass directly through the diluted acid and milky solution. If the solution has been made clear by muriatic acid, the operator can add, when the greater part of the antimony has been precipitated as sulphuret, a sufficient quantity of water, to prevent the action of the muriatic acid on the precipitate. The addition of the sulphuretted hydrogen gas is then to be continued till the precipitation is finished.

Separation from the Oxides of Nickel, Cobalt, Zinc, Iron, and Manganese.—When, on the contrary, the oxides of antimony are to be separated from the oxides of nickel, cobalt, zinc, iron, and manganese, then tartaric acid may be added to the acid solution before the sulphuret of antimony is thrown down by sulphuretted hydrogen gas. From the solution filtered from the sulphuret of antimony, the oxides in solution cannot be precipitated by their usual precipitants, in consequence of the presence of the tartaric acid. The solution is, therefore, supersaturated with ammonia, and the oxides are precipitated as sulphurets, by the addition of bihydrosulphuret of ammonia. This precipitate is dissolved, and the quantity of the oxides existing in the resulting solution is determined by the processes which have been described in preceding sections.—Of the substances above mentioned, the most difficult of estimation is the oxide of nickel, which cannot be effectually precipitated by bihydrosulphuret of ammonia. When, therefore, oxide of nickel is present, the operator must either observe the measures of precaution detailed at page 91, respecting the precipitation of oxide of nickel as sulphuret, or, instead of that, he must effect the separation of antimony from nickel in solution, as he would that of antimony from earths and alcalies; namely, without the addition of tartaric acid.

Separation from Manganese, Iron, Zinc, Cobalt, Cadmium, Lead, Bismuth, Copper, Silver, and Mercury, by Bihydrosulphuret of Ammonia.—The oxides which are precipitable from acid solutions by sulphuretted hydrogen gas, can be separated from antimony by treatment with bihydrosulphuret of ammonia, in which all the sulphurets of antimony are soluble. In the same manner, can also the metallic oxides which are only precipitable as sulphurets from neutral or alcaline solutions by bihydrosulphuret of ammonia, be separated from the oxides of antimony. The method of operating is as follows: The oxidised, or the metallic compound, is dissolved in a small matrass, in concentrated muriatic acid, or, if it is insoluble in that acid, in aqua regia. The concentrated solution is supersaturated with ammonia, which commonly produces a very large precipitate, inasmuch as nearly every thing is precipitated. This operation is performed in the matrass. After the precipitation by ammonia, a sufficient quantity of bihydrosulphuret of ammonia is added, and the matrass is corked. In general, this produces, in the cold, a bulky blackish brown precipitate; for, at first, a very large proportion of the sulphuret of antimony produced, precipitates with the other insoluble sulphurets; but, upon being digested at a gentle heat, the precipitate decreases in volume, and becomes blacker in colour. The more free sulphur the bihydrosulphuret of ammonia contains, the better is the separation effected; because the sulphuret of antimony is then much more easily dissolved. It is, therefore, a good plan, to dissolve pulverised sulphur in the bihydrosulphuret of ammonia, before adding it to the solution. When neither manganese, zinc, nor cadmium is present, and the precipitate has become quite black, the whole can be permitted to cool, in order that it may be filtered: it is previously necessary, however, to add water to the mixture. The filtration and edulcoration must follow one another without interruption; and the latter must be effected, not with pure water, but with a mixture of water and bihydrosulphuret of ammonia. The filtered solution contains all the antimony, in the state of sulphuret of antimony. This is precipitated by muriatic acid, with which the solution is cautiously acidulated. The precipitated sulphuret of antimony contains an admixture of sulphur, the presence of which is due to the decomposition of the excess of bihydrosulphuret of ammonia. The solution is allowed to remain over the precipitate, in a situation where it is exposed to an extremely gentle heat, until it no longer smells of sulphuretted hydrogen. The sulphuret of antimony is then filtered upon a weighed filter, and dried. When dry, it is weighed, and afterwards analysed according to one of the methods which have been described above.—The metallic sulphurets precipitated by the bihydrosulphuret of ammonia are dissolved and separated from one another by the methods which have been already described.—It is proper to observe here, that it is altogether indispensable to dissolve the compound which is to be analysed in muriatic acid, and to supersaturate the solution with ammonia, preparatory to treating it with bihydrosulphuret of ammonia. This is necessary, even when the compound is oxidised. If, instead of preparing the solution in this manner, the compound were to be very finely pulverised, and then submitted directly to the action of bihydrosulphuret of ammonia, the operation would fail, because perfectly dry oxides cannot be, in this manner, completely converted into sulphurets.

The metals which can be separated from antimony by the above process, are the following: Manganese, iron, zinc, cobalt, cadmium, lead, bismuth, copper, silver, and mercury. When mercury is combined with the antimony, the mixture of the metallic solution with the bihydrosulphuret of ammonia must be perfectly cold, and be allowed to repose for a considerable time before it is filtered. What is here said with respect to the metals, applies equally well to their oxides.

Separation from Cobalt, Nickel, Lead, Copper, Silver, Platinum, and Gold, by Chlorine Gas.—Another method of separating metallic antimony from most other metals, is the following: The alloy is placed in an apparatus, similar to that described at page 77, and is subjected to the action of a current of chlorine gas. The glass bulb *e*, to each side of which a glass tube is soldered, is weighed, first empty, and then with the substance to be analysed. One of the glass tubes is then bent at a right angle, the apparatus is placed together, and the bent tube is passed into the flask *k*. This flask contains a weak solution of tartaric acid, mixed with muriatic acid. There must be so much of this solution as to occupy one-half or one-third of the capacity of the flask. The glass tube passes a little way below the surface of the liquid. When the apparatus is full of chlorine gas, the glass bulb is very cautiously warmed. The metals are then converted into chlorides; the volatile chloride of antimony distils over, and is decomposed by the solution in the flask. The tartaric and muriatic acids, provided they are present in sufficient quantity, prevent the solution from becoming milky. When no more volatile matter is disengaged, the bulb is allowed to cool. The greater part of the bent glass tube is then cut from the bulb, and is accurately washed with water; the washings being poured into the flask *k*. This solution is then diluted with water, and the antimony it contains is precipitated in the state of sulphuret by sulphuretted hydrogen gas. The quantity of the other metals is next ascertained by weighing the chlorides which remain in the glass bulb. The weighing, however, is useless, when the alloy submitted to examination contained copper or any other metal, of which the quantity cannot be calculated from the weight of the resulting chloride. The weighing is performed either by taking the weight of the bulb and its contents, after a portion of the bent glass tube has been cut off, then dissolving the chlorides in water, and again weighing the empty bulb, or, on the contrary, by weighing the bulb and its contents with the portion of the glass tube which was cut off, after the latter has been washed and dried; the weight found in the latter case, immediately indicates the weight of the chlorides, because the separate weight of the glass apparatus was determined at the beginning of the experiment. This last method of proceeding is particularly proper to be adopted, when the chlorides in the bulb are such as are insoluble in water and in acids, such, for example, as chloride of silver. The analysis of the chlorides is performed according to the rules which are given in the preceding pages. If chloride of silver is contained in the glass bulb with other chlorides, it is treated with water and a little acid, for which purpose it is best to employ muriatic acid: a large quantity of water is then added, the whole is warmed, and the solution is filtered from the undissolved chloride of silver, which is afterwards weighed with proper precaution. The remaining metals are now precipitated from the solution, according to methods already described.—Antimony can be separated, in this manner, from cobalt, nickel, lead, copper, silver, platinum, and gold. When lead is present, however, the bulb dare not be too strongly heated.

This method is, nevertheless, not so much to be recommended as that according to which antimony is precipitated from solutions by sulphuretted hydrogen gas, or in which it is dissolved by an excess of bihydrosulphuret of ammonia. But this method, as will be shown farther on, is of the greatest advantage, and preferable to all others, when sulphuret of antimony is to be separated from other metallic sulphurets. The metallic alloys are, however, more difficultly decomposable than metallic sulphurets by gaseous chlorine. It very often occurs, in the analysis of alloys by chlorine gas, that the fixed chloride, when fusible, forms a coating over small particles of the undecomposed compound, and protects them from the action of the gas. This is particularly the case when the alloy cannot be pulverised.

Separation from Silver by Cupellation.—Some analysts have attempted to separate antimony from many metals; namely, from silver, by heating the alloy on a cupel in the muffle of an assay furnace. The antimony then becomes oxidised to oxide of antimony, which flies away in smoke, while the silver remains behind, and can be weighed. Yet, when an alloy which contains merely silver and antimony is ignited in this manner on a cupel of bone-ashes, until no more antimony smoke is observable, the regulus of silver produced, according to VON BONSDORF (SCHWEIGGER'S Jahrbuch, B. XXXIV. p. 235), is grey and dull at the surface, and contains still about one per cent. of antimony; on which account, it does not completely dissolve in nitric acid. But, when the resulting regulus is again cupelled with about five times its weight of pure lead, the operation being continued till the silver acquires its characteristic brilliancy, the resulting regulus of silver is quite free from antimony.

Separation from Tin.—The metals which have been treated of in the preceding sections, can be separated from antimony by a variety of processes; partly, by precipitating the sulphuret of antimony by passing sulphuretted hydrogen gas through an acid solution; partly, by dissolving the sulphuret of antimony in an excess of bihydrosulphuret of ammonia; partly, by treating the compounds with chlorine gas, and volatilizing the chloride of antimony. But it is impossible, by any of these methods, to separate tin from antimony, or oxide of tin from oxide of antimony; nor is there any other method yet known of separating these two metals with certainty. If both are in a reguline state, then, according to CHAUDET (*Annales de Chimie*, T. III. p. 376), the separation can be effected as follows: The operator must first assure himself that no other metals than tin and antimony are contained in the alloy. He must then determine in about what proportion these two metals are combined together. The easiest way to do this, is, to melt together quickly, one part of the alloy with twenty parts of tin, to roll out the melted alloy, and to boil it for some time with concentrated muriatic acid: what remains undissolved, shows approximatively, the quantity of antimony contained in the alloy. The operator then, with the greatest precaution, melts the alloy for examination with so much pure tin, that the proportions of tin and antimony contained in the new alloy, shall be as 20 to 1. The fusion is conducted as follows: The weighed metals are wrapped up in paper, placed in a little melting-crucible, and covered with a stratum of charcoal powder, to prevent oxidation; the metals are then heated red-hot for ten minutes. The crucible is then allowed to cool, the metallic bead is brushed and flattened, and the plate produced is cut into several pieces. These pieces are all wrapped up in paper, placed in the crucible, covered with charcoal powder, and again heated as long as before. This second fusion is necessary, to give uniformity to the alloy. The bead of metal must be again brushed very clean, rolled out into a very thin plate, and cut with scissars into several pieces. The operator then weighs out such a portion of this alloy as he wishes to submit to examination. This is to be boiled in a matrass, with an excess of strong muriatic acid, for at least two hours and a half. The solution is diluted with water, and filtered; the finely-divided antimony is thus gathered upon a weighed filter, upon which it can be dried and weighed. The quantity of the tin is reckoned from the loss.—This method is grounded upon the fact, that antimony, which even when alone is but very difficultly soluble in muriatic acid, becomes quite insoluble therein, when it is combined with much tin.

When other metals are combined with the tin and antimony, then an alloy of this kind, upon being treated with muriatic acid, can give other results. But lead may be combined in large quantity with these two metals, without prejudice to the accuracy of the experiment.

Separation of the Oxides of Antimony from one another.—When a solution contains several of the oxides of antimony, and their respective quantities are required to be estimated, the analysis is accompanied by such difficulties, as are scarcely to be overcome. If the operator should attempt to precipitate all the antimony by sulphuretted hydrogen gas after acidulating the solution, he must, in this case, take care that no tartaric acid be present; for, otherwise, the hope of finding the key to the quantity of oxygen in the dissolved oxides, in the weight of the resulting compounds of sulphur and antimony, would be vain. The presence of tartaric acid affects the nature of the precipitate. If, for example, it be contained in a solution with antimonious acid, the sulphuret of antimony which then precipitates, is not equivalent to antimonious acid, but to antimonic acid.

No method has yet been discovered of accurately determining the quantities of the different oxides of antimony when several of them exist together in solid compounds.

XXXIV. TUNGSTEN.

Quantitative Estimation as Tungstic Acid.—When tungsten is contained in a solution, in the state of tungstic acid, it is, according to BERZELIUS (POGGENDORFF'S Annalen, B. VIII. p. 272), best to effect its quantitative estimation by the process which follows: The concentrated solution, which may be either neutral or alcaline, is mixed with an excess of bihydrosulphuret of ammonia; upon which, sulphuret of tungsten is produced, and dissolved.

The solution is then mixed with diluted nitric acid, and is allowed to repose until it no longer smells of sulphuretted hydrogen gas. All the tungsten is thereby precipitated in the state of sulphuret of tungsten, which exhibits a yellow colour. The precipitate is filtered and washed with water, acidulated by a small quantity of muriatic acid, because pure water would partly dissolve it. After washing, the sulphuret of tungsten is dried and roasted by a gentle heat; it is thus converted into tungstic acid, which can be weighed.

Separation of Tungstic Acid from most Oxides, Earths, and Alcalies.—The tungstic acid can be separated in this manner from nearly all the oxides which have been treated of in the preceding sections. When it is combined with alcalies or earths, the compound to be analysed must not be decomposed by the direct application of nitric acid, which has the property of immediately precipitating the tungstic acid. The reason why nitric acid must not be so employed, is, that the resulting tungstic acid is never pure, but, according to BUCHOLZ (SCHWEIGGER'S Jahrbuch, T. III. p. 1), contains, not only nitric acid, but also alcali. The tungstic acid must be precipitated from such compounds, in the state of sulphuret of tungsten, by the process given above.

Analysis of Minerals containing Tungsten.—When tungstic acid is combined with other substances in such a manner that the compounds are indecomposable by acids, they must be levigated, and then fused with carbonate of potash in a platinum crucible. The fused mass is softened with water, which dissolves the tungstate and undecomposed carbonate of potash, and leaves the oxides with which the tungstic acid was previously combined, undissolved; unless, indeed, these oxides be soluble in a solution of carbonate of potash. The solution containing the tungstic acid is treated with bihydrosulphuret of ammonia, in the manner which has been described above.—When tungstic acid is combined with oxides, whose chlorides are soluble in water, as it is, for example, in the mineral called wolfram; the analysis can then, according to WÖHLER (POGGENDORFF'S Annalen, B. II. p. 345), be performed in a different manner: In this case, one part of the finely-levigated compound is fused with two parts of water-free chloride of calcium, in a platinum crucible. The melted mass is then boiled with water, upon which tungstate of lime remains undissolved. This is filtered and weighed. The metal is then precipitated from the filtered solution.

XXXV. MOLYBDENUM.

Quantitative Estimation as Molybdic Acid.—Molybdenum cannot be completely separated from its solutions by any reagent whatever. It can be best estimated by the method employed to estimate tungsten. The concentrated solution of molybdenum is treated with an excess of bihydrosulphuret of ammonia, in which the resulting sulphuret of molybdenum dissolves. Muriatic acid is added to this solution, and the whole is permitted to repose until the smell of sulphuretted hydrogen is no longer observable. The molybdenum is thus precipitated as sulphuret of molybdenum. If the operator intends to roast this precipitate in the same way as the sulphuret of tungsten, in order to convert it into molybdic acid, he must go to work very cautiously; for molybdic acid, when heated to redness in contact with air, is apt to sublime. It is better, therefore, to ignite the sulphuret of molybdenum in a little weighed retort, whereupon sulphur is volatilized, and the compound is converted into the lowest sulphuret, or grey sulphuret of molybdenum. It is less to the purpose to dry the precipitated sulphuret of molybdenum on a weighed filter, which can only be done in a vacuum over sulphuric acid, as it would become oxidised if dried in the open air, and then to digest a weighed portion of the dried sulphuret in aqua regia. The molybdenum is thereby converted into molybdic acid, which dissolves in the aqua regia. The sulphur partly precipitates, and is partly converted into sulphuric acid. The separated sulphur is filtered upon a weighed filter, then dried and weighed. From the filtered solution, the sulphuric acid is then precipitated by a solution of chloride of barium; and the quantity of sulphur is calculated from the weight of the resulting sulphate of barytes. When, now, the quantity of the sulphur contained in a weighed quantity of the sulphuret of molybdenum has been thus determined, it is easy to find the quantity of the molybdenum from the loss. But the quantity of the dissolved molybdic acid could also be estimated by saturating with ammonia the liquid filtered from the sulphate of barytes, whereupon molybdate of barytes would precipitate. But this operation, according to BERZELIUS (POGGENDORFF'S Annalen, B. VII. p. 280), is insufficient to cause the entire precipitation of the molybdic acid; and the operator has, moreover, the task of determining how much barytes is contained in the resulting molybdate of barytes; for, without examination, it is impossible to ascertain which of the compounds of molybdic acid and barytes is obtained. From the weight of the sulphuret of molybdenum, it is impossible, for reasons which are very evident, to calculate the quantity of molybdenum: for, supposing the sulphuret of molybdenum to have been precipitated by an acid from its solution in bihydrosulphuret of ammonia, it will of course be contaminated by sulphur precipitated at the same time.

Separation of Molybdic Acid from Metallic Oxides.—Molybdic acid can be separated, by bihydrosulphuret of ammonia, from most of the oxides which have been treated of in the preceding sections. The molybdic acid compound is dissolved in an excess of some acid; for which purpose, however, nitric acid is not fit to be employed. The solution is rendered ammoniacal, and is digested with an excess of bihydrosulphuret of ammonia. The metallic sulphurets thus precipitated, are filtered from the solution of the sulphuret of molybdenum; and the molybdenum is precipitated from the filtered solution by muriatic acid.—This method must likewise be employed when the molybdenum is combined with metallic oxides which cannot be precipitated from acid solutions by sulphuretted hydrogen gas; because, in this process, the molybdic acid is not converted by sulphuretted hydrogen gas into sulphuret of molybdenum.

Separation from Earths and Alcalies.—When molybdic acid is combined with an earth or an alcali, the solution is first treated with an excess of bihydrosulphuret of ammonia; sulphuret of molybdenum is then precipitated by the addition of muriatic acid, and the earth or alcali is afterwards separated from the filtered solution. But the salt can also be decomposed by the addition of nitric acid, and the evaporation of the solution to dryness. The molybdic acid is thereby separated, and upon treating the mass with water, remains undissolved, while the earthy or alcaline nitrate forms a solution.

XXXVI. CHROMIUM.

Precipitation of Oxide of Chromium.—When chromium exists in a solution, in the state of green oxide of chromium, the best way to precipitate it, is by means of caustic ammonia. It is thereby precipitated in the state of hydrate. The precipitate is washed, dried, ignited, and weighed. In the ignition of oxide of chromium, a certain degree of precaution is to be taken; because, when it is heated to a particular point, it suddenly becomes incandescent, and a slight explosion takes place, by which, when the quantity of the oxide is at all considerable, a portion of it may be thrown from the vessel and lost. It is therefore necessary to ignite the oxide of chromium in a platinum crucible, which can be accurately closed by a cover. The ignition renders it insoluble in acids.—The liquid, filtered from the hydrate of oxide of chromium, still contains a little oxide of chromium in solution. To obtain this, the solution must be evaporated to dryness, and the dry mass be treated with water, upon which the small portion of oxide of chromium remains undissolved, and can be collected and weighed.

Precipitation of Chromic Acid.—Reduction of Chromic Acid to Oxide of Chromium.—When chromium exists in a liquid in the state of chromic acid, the operator can precipitate it, when the solution is neutral, by a solution of nitrate of barytes, or when it is somewhat acid, by a solution of nitrate of lead; the one precipitant produces chromate of barytes, the other, chromate of lead, which is not soluble in very dilute acid solutions. From the weight of the ignited precipitate, the quantity of the chromic acid can be calculated.—The precipitation of chromic acid can also be effected by a solution of protonitrate of mercury, the solution of chromic acid having been previously neutralised. The resulting chromate of protoxide of mercury is submitted to ignition, which converts it into green oxide of chromium, from the weight of which oxide, the quantity of chromic acid is reckoned. The operator obtains a more accurate result, however, when the chromic acid is converted into oxide of chromium in the solution, and the quantity of the chromic acid is calculated from the weight of the oxide of chromium obtained by precipitation and ignition. The reduction of chromic acid to oxide of chromium, is best effected by muriatic acid. The chromic acid solution, if very dilute, must be somewhat concentrated by evaporation; it must then be mixed with an excess of muriatic acid, and boiled: during the boiling, the wished-for change occurs, the oxide of chromium remaining dissolved in the muriatic acid solution. Chlorine is meanwhile set free, and flies off in the state of gas. The reduction is promoted by the addition of alcohol; in that case, not chlorine gas, but chlorine ether, is disengaged. The excess of alcohol is expelled by the application of a gentle heat, which causes its evaporation. The oxide of chromium is then precipitated by ammonia.—Chromic acid can be converted into oxide of chromium, by another process, which consists in passing a current of sulphuretted hydrogen gas through the chromic acid solution; the oxide of chromium continues dissolved, when another acid has been added to the solution. Sulphur precipitates during this operation. The solution is warmed to expel the excess of sulphuretted hydrogen, and the sulphur is then separated by filtration. The oxide of chromium is then precipitated from the filtered solution by caustic ammonia. The reduction of chromic acid to oxide of chromium by sulphuretted hydrogen gas, is a process particularly proper to be adopted, when the chromic acid solution is very dilute. It is then, however, indispensably necessary to expose the solution to heat, after having passed a sufficient quantity of sulphuretted hydrogen gas through it. The object of this is, to separate the sulphur properly.

Separation from Alcalies and Alcaline Earths.—The separation of oxide of chromium and of chromic acid from other substances, is often accompanied by difficulties; because the chromium cannot be precipitated as sulphuret of chromium, either from acid solutions by sulphuretted hydrogen gas, or from neutral solutions by bihydrosulphuret of ammonia.—When the compounds to be examined are soluble in acids, the oxide of chromium can be separated from the alcalies and alcaline earths by ammonia, precisely in the same manner as peroxide of iron, with which oxide of chromium has many properties in common, can be separated from the same bases by the same reagent. If it be chromic acid which is combined with these bases, it must first be converted by muriatic acid or sulphuretted hydrogen gas, into oxide of chromium.

Separation from Magnesia.—No accurate method of separating oxide of chromium from magnesia is yet known. The operator might add to the solution of the two substances, a large quantity of muriate of ammonia, and then precipitate the oxide of chromium by ammonia, which would leave the magnesia still in solution.

Separation from Alumina.—Oxide of chromium is separated from alumina by caustic potash, which dissolves the alumina and leaves the oxide of chromium untouched. But it is indispensably necessary to boil the mixture of the two substances with caustic potash, during a considerable time; because an excess of caustic potash dissolves oxide of chromium in the cold, and it is only after a long boiling that the oxide of chromium is again precipitated. The alumina is obtained from the solution, filtered from the oxide of chromium, by first supersaturating the solution with muriatic acid, and then precipitating it with ammonia or carbonate of ammonia. When chromic acid is to be separated from alumina, it must first be converted into oxide of chromium. Oxide of chromium often occurs in combination with alumina, in the chrome-iron ore.

Separation from the Oxides of Manganese, Zinc, Cobalt, Nickel, and Iron.—The separation of oxide of chromium and of chromic acid, from the oxides of manganese, zinc, cobalt, and nickel, but in particular from those of iron, is accompanied by many difficulties. From such of these oxides as are soluble in an excess of ammonia, for example, from oxide of zinc, the oxide of chromium might, of course, be separated by ammonia: it has not yet been ascertained, however, whether the separation thus effected be accurate or not.

Most of these oxides, namely, peroxide of iron and protoxide of iron, can be separated from oxide of chromium by a process similar to that employed to separate the oxides of iron from zirconia and titanic acid. This process has been described at pages 58 and 170. The operator adds to the solution, so large a quantity of tartaric acid, that, upon subsequently supersaturating it with ammonia, neither oxide of chromium nor the oxides of iron are precipitated. He then subjects the clear ammoniacal solution to the action of bihydrosulphuret of ammonia, which produces a precipitate of sulphuret of iron. The vessel is placed in a rather warm situation, till the precipitate has fully subsided. The solution is then filtered, and the sulphuret of iron is washed with a mixture of water and bihydrosulphuret of ammonia. After being washed, the sulphuret of iron is converted into peroxide of iron, by the process described at page 54. The solution filtered from the sulphuret of iron contains the oxide of chromium; the estimation of which can be effected only by evaporating the solution to dryness, and afterwards igniting the dry mass till nothing but oxide of chromium remains. The ignition must be effected in a counterpoised platinum capsule, and with perfect access of atmospheric air. The operation is best performed, as has been intimated at page 59, by setting the platinum capsule in the muffle of an assay furnace; for it is difficult completely to burn away the charcoal of the tartaric acid, by using any other sort of fire place. When the tartaric acid made use of, is pure, so is, also, the resulting oxide of chromium. But when the tartaric acid contains lime, which is almost always the case with the tartaric acid found in commerce, then the whole quantity of that earth remains behind with the oxide of chromium. It is then necessary, since the impure oxide of chromium has been rendered insoluble in acids by the ignition it has been exposed to, to mix it with carbonate of potash, and to fuse it in a platinum crucible; then, to dissolve the fused mass in an excess of muriatic acid, to boil the solution, and to precipitate the pure oxide of chromium by caustic ammonia.

Separation from the Oxides of Iron by Caustic Potash.—The oxides of iron, as well as other metallic oxides which are completely precipitable by a solution of carbonate of potash, can be separated from oxide of chromium by the process which follows: The compound of the two oxides which are to be separated, is fused in a platinum crucible with an excess of carbonate of potash. The oxide of chromium is then, like the oxide of manganese, more highly oxidised by the air, and a production of chromate of potash takes place. When the crucible is cold, the ignited mass is treated with water; the chromate of potash and the excess of carbonate of potash dissolve in the water, while the peroxide of iron remains undissolved, and can be gathered upon a filter. The filtered solution is cautiously acidulated by muriatic acid, and is then boiled till the chromic acid is reduced to oxide of chromium; the oxide of chromium is then precipitated by ammonia. The peroxide of iron is dissolved in muriatic acid, and likewise precipitated from the solution by ammonia.

Analysis of Chrome-Iron Ore.—In this manner, however, the compound of oxide of chromium with protoxide of iron, which occurs in nature, and is known to mineralogists by the name of chrome-iron ore, cannot be analysed. The reason of this is, that that mineral is indecomposable by carbonate of potash; even when the mineral has been very finely levigated, fusion with carbonate of potash is almost entirely without effect. To decompose it for technical purposes, it is fused with nitrate of potash; yet this method cannot be employed in a quantitative analysis, since the fusion can be performed, neither in the platinum crucible nor in a silver crucible. The only way to proceed, when the operator is desirous of effecting a quantitative analysis of chrome-iron ore, is, to reduce the mineral, by levigation, to the finest state of division which is possible, and then to fuse it with caustic potash. In this operation, the same precautionary measures have to be observed as are requisite in the treatment of siliceous substances by caustic potash. As these precautionary measures will be circumstantially described, in the section on Silicium, it is unnecessary to speak of them at length here.—After the fusion with caustic potash, the mass is treated with water, which dissolves the resulting chromate of potash and the excess of caustic potash. The peroxide of iron which remains undissolved is, after filtration, dissolved in muriatic acid; in general, it leaves a small portion of undecomposed chrome-iron ore, which does not dissolve in the acid which dissolves the peroxide of iron. This small quantity of the undecomposed compound is filtered from the solution of peroxide of iron; it is then dried and weighed, and the weight is deducted from that of the whole quantity of chrome-iron ore submitted to analysis. The peroxide of iron is precipitated by ammonia, and the precipitate is weighed. The chromic acid existing in the solution of chromate of potash, is reduced to oxide of chromium, and is then also precipitated by ammonia.—When the chrome-iron ore contains alumina, which is very frequently the case, then the alumina is found in the solution of chromate of potash, supposing that a sufficient quantity of the caustic potash has been employed. The solution is then, in the same manner, acidulated by muriatic acid, and the chromic acid is reduced to oxide of chromium; the latter is thereupon separated from the alumina, by the process which has been described above. —The oxidised iron which is contained in the chrome-iron ore cannot be reduced by hydrogen gas, not even when it is, at the same time, exposed to a very strong heat. It is consequently not possible satisfactorily to determine the state of oxidation of the iron, in the chrome-iron ore, by following the process which has been described at page 64.

Separation from Deutoxide of Copper, Protoxide of Lead, and Oxide of Silver.—The oxides which are precipitable from acid solutions by sulphuretted hydrogen gas, can be easily separated from oxide of chromium and chromic acid; such, for example, is the deutoxide of copper. The oxide of chromium is not affected by sulphuretted hydrogen gas, while the chromic acid is converted thereby into oxide of chromium, which remains dissolved in the acid solution. Protoxide of lead can be extremely well separated from oxide of chromium, by converting both oxides by means of muriatic acid, into chlorides, and then treating the chlorides with alcohol. The chloride of lead remains undissolved by the alcohol, while the protochloride of chromium dissolves therein. After evaporating the alcohol by the application of a gentle heat, the oxide of chromium can be precipitated from the solution by caustic ammonia. —When chromic acid is combined with protoxide of lead, the compound is boiled with a mixture of muriatic acid and alcohol; whereupon, the chromic acid is converted into oxide of chromium, under disengagement of chlorine ether. The oxide of chromium dissolves in the muriatic acid, while the chloride of lead precipitates in the spirituous liquid. The chloride of lead is filtered on a weighed filter, and washed with spirits of wine; it is then dried and weighed. The quantity of protoxide of lead is calculated from the weight of the chloride of lead. The latter can also be converted into sulphate of lead, and the quantity of protoxide of lead be estimated in that manner.—It is very easy to examine, by this process, not only the chromate of lead which is found in commerce, but that which occurs in nature and is known to mineralogists by the name of red lead-ore. It is necessary, however, in the analysis of the red lead-ore, previously to levigate the compound very finely, since, otherwise, the muriatic acid does not fully decompose it.—Oxide of silver can likewise be separated from the oxides of chromium by muriatic acid.

Separation of Chromic Acid from Oxide of Chromium.—When chromic acid is to be separated from oxide of chromium, and the two compounds are in solution, the way to proceed is, according to MAUS (POGGENDORFF'S Annalen, B. IX. p. 127), to add a solution of acetate of lead: whereby chromate of lead is precipitated, while the oxide of chromium and the excess of acetate of lead, remain in solution. Care must be taken, that the solution does not contain so much free acid, as to act as a solvent on the chromate of lead. Acetic acid may be present in excess without prejudice, since the chromate of lead is insoluble in that acid.—When a solid compound of chromic acid and chromic oxide is to be examined, it may, when it has been recently precipitated, be digested with a solution of acetate of lead, to which a little free acetic acid has been added. The operator obtains a solution of the oxide of chromium, while chromate of lead remains undissolved. The excess of lead is separated from the solution of oxide of chromium by a current of sulphuretted hydrogen gas; the oxide of chromium can then be precipitated. It is necessary to decompose the resulting chromate of lead, that it may be determined how much chromic acid it contains. The best way to decompose it, is by means of muriatic acid and alcohol. The chloride of lead is separated by filtration, and the oxide of chromium is precipitated from the filtered solution. The quantity of chromic acid is ascertained by calculation.

XXXVII. ARSENIC.

Quantitative Estimation of the Acids of Arsenic, by Protoxide of Lead.—The quantitative estimation of the arsenious and arsenic acids in solution, can be effected by various operations. If the solution, besides arsenic acid, contains only nitric acid, and no description of fixed substance, it must be mixed with an accurately weighed quantity of freshly ignited pure protoxide of lead. The solution must then be evaporated to dryness, and the remainder be ignited in a little counterpoised platinum capsule. The quantity of the arsenic acid is learned, by deducting the weight of the protoxide of lead employed, from that of the ignited mass. It is necessary to observe here, that the solution must contain no other acid than arsenic acid, capable of producing a fixed salt with protoxide of lead. The presence of ammonia is likewise disadvantageous in this method of estimation.

Quantitative Estimation of Arsenious Acid: Precipitation by Sulphuretted Hydrogen Gas.—Arsenious acid cannot be easily converted into arsenic acid, by means of nitric acid alone, but only by means of aqua regia. But arsenic acid cannot be quantitatively estimated by protoxide of lead, in the manner described above, if muriatic acid is present in the solution. It is better therefore to precipitate the arsenic from the solution, by a current of sulphuretted hydrogen gas. The sulphuret of arsenic, precipitated from diluted acid solutions, in such a case, is equivalent in the proportion of its constituents to the arsenious acid. The gas is allowed to stream through the solution, till the latter is fully saturated therewith. The solution is afterwards permitted to remain in a situation where it may be very moderately warmed, until the smell of sulphuretted hydrogen is no longer perceptible. By this means, the last traces of sulphuret of arsenic, which remain dissolved in a solution saturated with sulphuretted hydrogen gas, are completely precipitated. The resulting sulphuret of arsenic is filtered upon a weighed filter, and washed; it is afterwards dried by a very gentle heat, and then weighed. If the operator were convinced that the solution contained only arsenious acid, he might calculate the quantity of the arsenious acid from the weight of the resulting sulphuret; nevertheless, an error might be committed, even in that case, because the precipitated sulphuret of arsenic contains more sulphur than, according to theory, it ought to contain; the reason of which is, that free sulphur is deposited during the decomposition of the excess of sulphuretted hydrogen gas which was dissolved in the solution. But when the operator imagines, that, in addition to the arsenious acid, a portion of arsenic acid was also present, the resulting sulphuret of arsenic must invariably be farther examined, which indeed, for the reasons above mentioned, should also be the case, when merely arsenious acid was present. The best method of examining the sulphuret of arsenic is the following: Let it be dried and weighed, and then put as much of it as can be separated from the filter, into a small matrass or glass: then weigh the filter with what remains upon it, to ascertain how much of the sulphuret of arsenic is submitted to experiment. Pour aqua regia over the sulphuret, and allow it to digest therewith. The arsenic is converted into arsenic acid; the sulphur is partly converted into sulphuric acid, and partly precipitated as pure sulphur. The digestion would be of too long continuance, and the aqua regia would require to be often renewed, if it were intended to convert the sulphur wholly into sulphuric acid. As soon, however, as the sulphur has concreted into a few lumps, it is filtered upon a weighed filter, and washed; then very carefully dried and weighed. To the filtered solution, a solution of chloride of barium is added; the quantity of sulphur contained in the solution, is calculated from the weight of the resulting sulphate of barytes. The two quantities of sulphur indicate the entire quantity contained in the sulphuret of arsenic submitted to analysis. The loss indicates the quantity of arsenic, from which the quantity of arsenious acid can be reckoned.—The precaution is hereby to be observed, of not filtering the undissolved sulphur, until it has digested a pretty long time with the aqua regia. The colour of sulphuret of arsenic does not strikingly differ from the colour of sulphur; yet, after a little experience, the operator learns to judge extremely well from the colour and appearance of the sulphur, whether or not it contain any sulphuret of arsenic.

Quantitative Estimation of Arsenic Acid.—In the same manner can arsenic acid in solution be quantitatively estimated by sulphuretted hydrogen gas; and this method is to be adopted when it is impossible to effect the estimation by protoxide of lead, as it is, for example, when the solution contains muriatic acid or fixed constituents. Arsenic acid, however, is precipitated by sulphuretted hydrogen gas far more slowly than arsenious acid. Of all substances that are acted on by sulphuretted hydrogen gas, arsenic acid is the one whose precipitation requires the greatest length of time. Besides this, a much greater quantity of the resulting sulphuret of arsenic remains in solution, in the hydrosulphuretted liquor, than is the case when the arsenious acid is precipitated. The dissolved sulphuret can, nevertheless, be fully precipitated, by exposing the mixture to a very gentle heat till it ceases to smell of sulphuretted hydrogen.—If the operator knows to a certainty, that the solution contained only arsenic acid, he may reckon the quantity of the acid from the weight of the sulphuret, since the sulphuret of arsenic produced in this case is equivalent to arsenic acid. It must, however, be remembered, that the precipitated sulphuret of arsenic is contaminated by free sulphur, produced by the decomposition of the excess of sulphuretted hydrogen. This free sulphur often amounts to some per cents, so that it is indispensably necessary to submit the sulphuret of arsenic thus obtained to analysis. The examination is conducted in the same manner as that of the sulphuret of arsenic precipitated from solutions of arsenious acid.

Treatment of Solutions of Arsenic, by Bihydrosulphuret of Ammonia.—Instead of estimating the quantity of arsenious or arsenic acid, by passing a current of sulphuretted hydrogen gas through their diluted solutions, the operation which follows may be adopted: The acid solution of arsenic is supersaturated with ammonia and mixed with a sufficient quantity of bihydrosulphuret of ammonia: hereupon, the sulphuret of arsenic which is formed, dissolves readily and completely in the excess of bihydrosulphuret of ammonia; it matters not, whether the sulphuret produced be equivalent in its composition to the arsenious or the arsenic acid. If the solution be very concentrated, it is diluted with water, and then mixed with as much muriatic acid as is sufficient to make it acid. Sulphuretted hydrogen gas is then disengaged, and sulphuret of arsenic precipitated. The solution is digested at a very gentle heat, until it no longer smells of sulphuretted hydrogen gas, and the sulphuret of arsenic is then filtered. It is absolutely necessary to analyse this sulphuret of arsenic in the manner which has been described above; for it contains a large proportion of free sulphur, furnished by the decomposed bihydrosulphuret of ammonia.

Precipitation of Arsenic Acid, by Salts of Lead.—The quantitative estimation of arsenic, by precipitating the arsenious and arsenic acids by sulphuretted hydrogen gas, and by analysing the resulting sulphuret of arsenic, is the only method which gives satisfactory results. In general, however, arsenic acid is precipitated as arseniate of lead, by solutions of acetate, or of nitrate of lead; the quantity of the arsenic acid being reckoned from the weight of the arseniate of lead. But this method affords results with which no analyst should be contented; setting the fact out of question, that, when other metals are present in the solution, this method is accompanied by more difficulties than the method described above. It being moreover necessary, when the operator wishes to have results that shall approach the truth, to ascertain how much arsenic acid is contained in the resulting arseniate of lead, this method comes to be more tedious than the quantitative estimation of arsenic, in the state of sulphuret.

Separation from Alcalies, Earths, and the Oxides of Manganese, Iron, Zinc, Cobalt, Nickel, Uranium, Titanium, and Chromium, by Sulphuretted Hydrogen Gas.—The substances which are not precipitable by sulphuretted hydrogen gas, can be separated thereby from the acids of arsenic. The diluted solution must be acidulated, and the gas be allowed to pass through, until the solution is completely saturated. The solution must then be exposed to a very gentle heat until it no longer smells of sulphuretted hydrogen. The precipitated sulphuret of arsenic is separated by filtration, and analysed in the manner which has been described above. The other substances are afterwards separated from the filtered solution. If peroxide of iron was present in the solution, the sulphuretted hydrogen gas will have converted it into protoxide of iron.—The oxide of arsenic can be separated in this manner from the earths and alcalies, and from the oxides of manganese, iron, zinc, cobalt, nickel, uranium, titanium, and chromium.

If the arsenic is combined in the metallic state with the above-named metals, the alloy must be dissolved in nitric acid or in aqua regia; the solution must then be diluted, and treated with sulphuretted hydrogen gas. It is, in general, better to treat the alloy with nitric acid than with aqua regia, because nitric acid produces chiefly arsenious acid, while aqua regia, on the contrary, chiefly produces arsenic acid; now, sulphuretted hydrogen gas precipitates arsenic acid with much more difficulty than arsenious acid.

Separation from the Oxides of Cadmium, Lead, Bismuth, Copper, Silver, and Mercury, by Bihydrosulphuret of Ammonia.—The oxides of arsenic can be separated from those of cadmium, lead, bismuth, copper, silver, and mercury, by bihydrosulphuret of ammonia. The solution, if acid, is rendered ammoniacal, and a sufficient quantity of bihydrosulphuret of ammonia is then added. When the quantity of arsenic is very considerable, the whole is allowed to digest at a gentle heat for a considerable time, an excess of bihydrosulphuret of ammonia being added, and the glass being covered with a glass plate. But it is better, with large quantities of arsenic, to operate the digestion at a stronger heat, in a matrass closed, but not quite air-tight, with a cork. When completely cold, the insoluble metallic sulphurets are filtered, and the precipitate is washed with a mixture of water and bihydrosulphuret of ammonia. These sulphurets are analysed, for the purpose of estimating the oxides they are equivalent to, by methods which have been given in the preceding sections. The filtered solution is acidulated by muriatic acid, and is allowed to digest at a gentle heat, until it no longer smells of sulphuretted hydrogen; the dissolved sulphuret of arsenic then precipitates. It is filtered upon a weighed filter, and weighed; after which, the quantity of sulphur it contains is ascertained, and the quantity of arsenic is then reckoned. The separation of arsenic from the above-named metals, by bihydrosulphuret of ammonia, is not effected completely, unless the insoluble sulphurets are digested sufficiently long with the bihydrosulphuret of ammonia.

Separation from the Oxides of Manganese, Iron, Zinc, and Cobalt, by Bihydrosulphuret of Ammonia.—The oxides of arsenic can, in the same manner, be separated from those of manganese, iron, zinc, and cobalt, whose sulphurets are quite insoluble in an excess of bihydrosulphuret of ammonia. This method is often preferred to that, according to which arsenic is separated from the above-named oxides, by passing a stream of sulphuretted hydrogen gas through the acid solution. But in this case also, the insoluble metallic sulphurets must be properly digested with the excess of bihydrosulphuret of ammonia; because they may otherwise retain small portions of sulphuret of arsenic. When the oxides of iron have been thus separated from the acids of arsenic, it happens very frequently, that upon dissolving the sulphuret of iron in muriatic acid, very small portions of sulphuret of arsenic remain behind undissolved. This is never the case, however, when the digestion with bihydrosulphuret of ammonia is operated with a proper degree of attention.

Separation from the Earths and Alcalies, by Bihydrosulphuret of Ammonia.—Bihydrosulphuret of ammonia is also employed to separate the acids of arsenic from the earths and alcalies. Before the reagent is added, the solution, if acid, must be rendered alcaline by ammonia. The sulphuret of arsenic is then precipitated by muriatic acid. The solution filtered from the sulphuret of arsenic, contains the earth or alcali separated from the arsenic or arsenious acid.

Separation of Arsenic Acid from Metallic Oxides by Caustic Potash.—It is customary, when metallic arseniates are dissolved in acids, to precipitate the metallic oxides they contain, by adding an excess of caustic potash. This method, however, ought never to be employed, when results approaching to truth are desired; for even when a base can be fully precipitated by alcalies, either caustic or carbonated, from its solutions in muriatic, nitric, sulphuric, or other volatile acids, its precipitation ceases to be effected when, at the same time, the solution contains arsenic acid. If so much of the alcali be added as is sufficient exactly to saturate the solution, then the arseniate precipitates: if more alcali be added, it abstracts indeed a portion of arsenic acid from the precipitate, but no excess of alcali, however great it may be, is sufficient to deprive the base of all its arsenic acid. Consequently, this method of separation is scarcely ever successful.

Decomposition of Arseniates by Nitrate of Lead.—Arsenic acid is often separated from bases and quantitatively estimated by the process which follows: The arseniate is dissolved in nitric acid, mixed with a solution of nitrate of lead, and cautiously evaporated to dryness: the excess of nitric acid is thus expelled, and when the mass is afterwards treated with water, the arseniate of lead remains undissolved, while the excess of nitrate of lead, and the base which was previously combined with the arsenic acid, but now is united to nitric acid, dissolve. The weight of the arseniate of lead is ascertained, and the quantity of the arsenic acid is calculated, too generally, on the supposition that the arseniate of lead is neutral. This supposition is, however, not correct. The operator must determine experimentally how much protoxide of lead is contained in the precipitated arseniate of lead. It is also necessary, if the quantity of the base is to be determined, to separate, in the first place, the excess of protoxide of lead from the filtered solution. It is easy to perceive that, as was observed in a preceding paragraph, this method does not deserve to be employed.

Separation of Arsenic Acid from Barytes, Lime, Strontian, and Protoxide of Lead, by Sulphuric Acid.—Some bases whose compounds with sulphuric acid are insoluble in water or in weak spirits of wine, can be separated from arsenic acid, by the following process, with great ease and accuracy. These bases are barytes, lime, strontian, and protoxide of lead. Supposing one of these bases to be combined with arsenic acid, and the compound to be presented for examination in the solid form, it is, in the first place, to be weighed. If it contain water, it must be heated to redness before it is weighed. It is then pulverised, and submitted to the action of sulphuric acid, with which it is allowed to digest for some time. Thereafter, if the base is barytes alone, water is added; and the sulphate of barytes is filtered, washed, and weighed. From the weight of the sulphate of barytes, the quantity of barytes is calculated. The quantity of the arsenic acid is then ascertained with great accuracy from the loss. If the base is lime, strontian, or protoxide of lead, then, after the decomposition of the compound by sulphuric acid, the mixture is diluted with spirits of wine, instead of water; because the sulphates of these bases are partially soluble in water, but not in spirits of wine, while the separated arsenic acid and the excess of sulphuric acid dissolve in spirits of wine as readily as in water. The sulphates are filtered, washed with alcohol, and weighed. The quantities of the respective bases are then calculated.

Before, however, these arseniates are digested with sulphuric acid, it is proper to treat them with muriatic acid. The neutral and basic arseniates are all soluble in muriatic acid; so are also the acid arseniates, when in a dry state. But most of the acid arseniates, which have earths or metallic oxides for bases, are often insoluble, even in concentrated muriatic acid. These can only be decomposed by being pulverised, and then boiled for a considerable length of time with concentrated sulphuric acid in a platinum capsule. Still, the boiling must not be continued so long as to drive away all the sulphuric acid. When, after cooling, the mass is treated with water, it completely dissolves, provided the base be not one of those which form insoluble, or nearly insoluble, compounds with sulphuric acid.

Decomposition of Arsenical Alloys by Chlorine Gas.—When a compound of reguline arsenic with other metals is to be examined, it is good to operate by means of gaseous chlorine. Most of the metals which alloy with arsenic can be separated therefrom by the process employed to separate antimony from the metals whose chlorides are not volatile. The description of this process will be found at page 183. The reguline compounds of arsenic are, however, far less easily decomposable by chlorine, than the compounds formed by the combination of the sulphurets of arsenic and antimony with other metallic sulphurets. The method of operating, in the decomposition of these compounds, will be described in the article on Sulphur. Even when but a few grammes* of an arsenical alloy are submitted to analysis, and chlorine gas is allowed to pass during a whole day over the heated compound, a portion of the alloy still often remains in the glass bulb undecomposed. And when, subsequently, the fixed chlorides are treated with water, for the purpose of dissolving them, if soluble, there remains, of course, the undecomposed portion of the compound, in an undissolved state. The quantity so remaining must be determined, and its weight deducted from that of the portion submitted to analysis. On account of the slowness with which arsenical alloys are decomposed by chlorine, this method is only worthy of adoption, when the metals to be separated are those whose oxides cannot be separated from the acids of arsenic either by sulphuretted hydrogen gas or bihydrosulphuret of ammonia.

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* A gramme is equal to 15,438 grains Troy.

Separation of Arsenic from Tin.—The separation of tin from arsenic is accompanied by difficulties which have not yet been overcome. No sure method of separating the two metals is known.

Separation of Arsenic from Antimony.—The separation of antimony from arsenic is likewise accompanied by many difficulties. If, however, the two metals are combined with one another in the reguline state, then the arsenic can be separated from the antimony, by applying heat and excluding the compound from atmospheric air, since, under these circumstances, the arsenic, but not the antimony, volatilizes. This method cannot be employed in the separation of arsenic from other metals; for most of these retain a part, and commonly the whole, of the arsenic combined with them, even when heated to redness; the arsenic, in such cases, cannot be entirely expelled, even by roasting the compound in the open air. To separate antimony from arsenic, the best method is to ignite the alloy in an atmosphere of hydrogen gas. For such an experiment, the apparatus represented at page 83 may be employed. When the quantity of arsenic is considerable, care must be taken that the hindermost glass tube attached to the glass bulb *g* be not too small in diameter. As soon as the apparatus is filled with hydrogen gas, the bulb *g* is heated. The heating is continued as long as metallic arsenic continues to sublime into the hindermost glass tube. As fast as the metallic arsenic is deposited in this tube, it must be driven forwards by the flame of a small spirit lamp, until it is entirely expelled from the tube.

When no more arsenic proceeds from the bulb, and when all has been driven from the tube, the apparatus is allowed to cool, the current of hydrogen gas being continually sustained. At the end of the experiment, the metallic antimony which remains in the bulb is weighed, and the quantity of arsenic is estimated from the loss. It is necessary to take care not to employ too strong a heat, lest the sublimed arsenic be accompanied by a little antimony. The operator will, of course, with a view to his health, take particular care, in the performance of this experiment, to avoid inhaling an atmosphere of arsenical vapours. The operation must not be performed in the open room, but under a chimney. Nearly all the varieties of the mineral called native arsenic (Scherbenkobalt), contain small quantities of antimony, capable of being separated by the process just described.

When, however, antimony and arsenic are dissolved in a liquid, or when they are combined with other substances, so as to be incapable of separation by the above process, it is then necessary to operate in a different manner. The solution of the two substances is diluted with a sufficient quantity of water; previous to which, however, it is mingled with tartaric acid, to prevent its becoming milky on dilution. If the substance to be examined is in the reguline state, it is dissolved in aqua regia, and the resulting solution is mixed with tartaric acid and diluted with water. A current of sulphuretted hydrogen gas is then passed through the solution, till it is completely saturated; and the solution is afterwards heated, to cause the entire precipitation of the sulphurets. When arsenic acid is contained in the solution, the operator can see very distinctly that what is first precipitated is sulphuret of antimony, and that the sulphuret of arsenic is not precipitated till after a considerable lapse of time: an orange-red stratum is first deposited at the bottom of the glass, and is afterwards covered by a bright yellow stratum. It is therefore necessary, before filtration, to mingle the two precipitates intimately with each other, which is done by industriously stirring the liquor with a glass rod. A weighed filter is employed for the filtration; and the sulphurets are dried upon it, by exposure to an extremely gentle heat, until they cease to decrease in weight. When the weight of the sulphurets has been determined, a portion thereof, about the half of the precipitate, is shaken into a glass. The remainder, with the filter, is again very cautiously warmed and weighed. By this means the operator learns how much of the sulphurets is taken for farther examination. The portion shaken into the glass is very cautiously oxidised by aqua regia. This operation is best performed in the manner described at page 176, in treating of the oxidation of the sulphuret of antimony. The solution produced by this operation is mixed with tartaric acid and diluted with water. If any sulphur precipitates, it must be filtered, dried, and weighed. The sulphuric acid, produced by the oxidation of the sulphurets, is precipitated from the filtered solution by a solution of chloride of barium. From the weight of the sulphate of barytes, the quantity of the sulphur is calculated. To this quantity must be added that of the sulphur which the aqua regia had failed to oxidise. When, by this process, the quantity of sulphur contained in a weighed portion of the metallic sulphurets has been determined, it is easy to perceive what must be the common weight of the antimony and arsenic; but a different operation is necessary to show the relative proportions of the two metals. Another portion of the precipitated sulphurets is heated in an atmosphere of hydrogen gas, precisely in the same manner as the sulphuret of antimony is heated when the object is to determine how much antimony it contains. A minute description of this operation will be found at page 177. A glass bulb, on each side of which a glass tube is soldered, is weighed. It is then filled with a suitable quantity of the dry metallic sulphurets. The glass tubes are then very carefully cleaned with the plume of a feather, and the whole is again weighed. By this means, the quantity of the sulphurets employed in the experiment is accurately determined. When the apparatus is placed together and is full of hydrogen gas, the glass bulb is heated, at first gradually, and then more powerfully. The excess of sulphur of the sulphuret of antimony is the first thing that flies off, after which the sulphuret of arsenic sublimes. A great part of the latter is converted, by the action of the hydrogen gas, into metallic arsenic. Care must be taken to expel all the sublimate from the tube, by applying the flame of a small spirit lamp. It is very necessary not to heat the bulb too powerfully or for too long a time, since otherwise a portion of antimony could be driven away with the sublimed arsenic; but it is also necessary not to employ too weak a heat, for then the reduction would be imperfect. When proper care is observed, this method affords a result with which the operator may be contented, although it is not perfectly accurate: in general, however, it is only about a half per cent. from the truth.—The antimony which remains behind is weighed. As the operator learns by this process the quantity of antimony contained in the precipitated metallic sulphurets, and has, by a previous operation, determined the quantity of sulphur, it is now easy to find the quantity of arsenic from the loss.

This method of separating arsenic from antimony is preferable to other methods which have been recommended for this purpose; for the results afforded by other methods are all more remote from the truth than those afforded by this method.—It is proper to sublime the sulphuret of arsenic in an atmosphere of hydrogen gas; because, in a common distillation, a portion of sulphuret of antimony, by no means inconsiderable, would sublime with the sulphuret of arsenic.

It is scarcely necessary to observe, that, in performing an experiment of this kind, the operator should take care not to inhale the arsenical vapours. The operation must, of course, be performed under a chimney, and not in an open room.

It will be immediately perceived, that, according to this method, the slightest quantity of antimony in sulphuret of arsenic can be more easily detected and weighed, than a slight quantity of arsenic in sulphuret of antimony.

Analysis of Alloys of Antimony and Arsenic with other Metals.—If the operator has a reguline compound of arsenic and antimony with other metals, or a compound of the oxides of arsenic and antimony with other oxides, it must be dissolved in aqua regia, or, if already oxidised, in muriatic acid. The solution is mixed with tartaric acid, diluted with water, and exposed to a current of sulphuretted hydrogen gas. The precipitate, thus produced, consists of sulphuret of antimony and sulphuret of arsenic, provided the other metals are not precipitable from acid solutions by sulphuretted hydrogen gas. The solution is filtered from the precipitate, supersaturated with ammonia, and mixed with bihydrosulphuret of ammonia. This precipitates the remaining metals; it is, moreover, the only method by which they can be precipitated; for the tartaric acid which is present in the solution, hinders the reaction of all other precipitants. What is most difficult in such a case as this, is to estimate the quantity of nickel; for it is well known that the precipitation of nickel by bihydrosulphuret of ammonia, is accompanied by great difficulties.—If, however, the metals combined with the antimony and arsenic are precipitable from acid solutions by bihydrosulphuret of ammonia, the separation must then be effected by bihydrosulphuret of ammonia.

Separation of the Oxides of Arsenic from each other.—The separation and quantitative estimation of the arsenious and arsenic acids, when both are contained together in a solution, is combined with such difficulties as have hitherto proved to be insurmountable. The arsenic might indeed be precipitated by sulphuretted hydrogen gas, and the sulphuret of arsenic be analysed, to find the relative equivalent proportions of oxygen and arsenic; for which the respective quantities appertaining to the arsenious and arsenic acids might be calculated. It must, however, be borne in mind, that results so obtained must be far wide of the truth; because the sulphuret of arsenic is always accompanied by free sulphur, produced by the decomposition of the sulphuretted hydrogen which existed in the solution: hence, all the reckoning is rendered uncertain.

XXXVIII. TELLURIUM.

Reduction by Sulphurous Acid.—If tellurium exists in a solution as oxide, and is to be quantitatively estimated, the best method of proceeding is to reduce it to the metallic state by sulphurous acid. The reduced tellurium is filtered upon a weighed filter, carefully dried by exposure to a gentle heat, and weighed repeatedly, until, on fresh exposure to heat, it no longer loses weight. Instead of a solution of sulphurous acid in water, it is better to employ a solution of sulphite of ammonia. If the solution of the oxide of tellurium is alcaline, it is acidulated by muriatic acid; so much of which must be added, that the oxide at first precipitated, redissolves in the excess of acid. The acid solution is warmed in a matrass until it gently boils; a little of the solution of sulphite of ammonia is then gradually added to the acid solution. The tellurium precipitates in the form of black powder. The only thing requiring to be particularly attended to here, is, to see that the solution always contains free muriatic acid. If the solution of the oxide of tellurium contains nitric acid, the result afforded by the reduction is uncertain; for the nitric acid set at liberty during the process can easily redissolve a portion of the reduced tellurium. To prevent this occurrence, the tellurium solution must, previous to the addition of the sulphite of ammonia, be gradually mixed with muriatic acid, and the mixture must then be concentrated by evaporation, till the nitric acid is completely destroyed. The way to know when the nitric acid is completely destroyed, is to take notice of the smell of the gas disengaged during the evaporation: if it have the most distant resemblance to chlorine, the nitric acid is not wholly destroyed. The gas must have the smell of pure muriatic acid before the operation is terminated. The concentrated solution is afterwards diluted with a little water, and the tellurium is then reduced by the sulphite of ammonia.

Precipitation by Sulphuretted Hydrogen Gas; Separation from the Earths and Alcalies, from the Oxides of Manganese, Iron, Zinc, Cobalt, Nickel, Uranium, &c.—The oxide of tellurium is precipitated from its acid solutions by sulphuretted hydrogen gas. The precipitate is brownish black sulphuret of tellurium. By this reagent, then, the oxide of tellurium can be separated from the earths and alcalies, and from the oxides of manganese, iron, zinc, cobalt, nickel, uranium, &c. The precaution should be observed here, of exposing the liquid, after effecting the precipitation, to a very gentle degree of heat, until it no longer smells of sulphuretted hydrogen gas. The precipitated sulphuret of tellurium is then filtered. If the operator is convinced that no other sulphuret has been precipitated with the sulphuret of tellurium, he may filter the latter upon a weighed filter, and after having dried and weighed it, may calculate the equivalent proportion of oxide of tellurium. But, in general, the sulphuret of tellurium is accompanied by an excess of sulphur, owing to the decomposition of the dissolved sulphuretted hydrogen by the oxygen of the atmosphere. The excess of sulphur is particularly great, when the solution contained peroxide of iron. In this case, the sulphuret of tellurium must, while still wet, with the filter, be digested in aqua regia: the tellurium then becomes oxidised, while the sulphur is partly deposited, and partly converted into sulphuric acid. The digestion is continued till the colour of the precipitated sulphur is perfectly yellow. The solution is then filtered; the nitric acid it contains is destroyed by the addition of a sufficient quantity of muriatic acid, and the tellurium is reduced by sulphite of ammonia.

When reguline tellurium is combined with metals, whose oxides are not precipitable from acid solutions, by sulphuretted hydrogen gas, the metallic compound is dissolved in nitric acid or in aqua regia; and the solution, after dilution with water, is treated with sulphuretted hydrogen gas. Strong nitric acid must be employed to dissolve the compound; for, if it be treated with weak nitric acid, a slight disengagement of telluretted hydrogen gas may take place.

Separation from the Oxides of Cadmium, Lead, Bismuth, Copper, Silver, and Mercury, by Bihydrosulphuret of Ammonia. —The oxide of tellurium can be separated from the oxides of cadmium, lead, bismuth, copper, silver, and mercury, by bihydrosulphuret of ammonia. The solution must be supersaturated with ammonia, the bihydrosulphuret of ammonia added in excess, and the whole allowed to digest for some time at a gentle heat. Thereupon, the sulphuret of tellurium easily dissolves, while the sulphurets of the other metals remain undissolved.—When metallic tellurium is combined with the metals of those oxides, the compound is dissolved in nitric acid or aqua regia; the solution is supersaturated with ammonia, and then treated as above. —The sulphuret of tellurium is precipitated from its solution in bihydrosulphuret of ammonia by muriatic acid; the solution is gently warmed, until it no longer smells of sulphuretted hydrogen; the sulphuret of tellurium is then filtered from the solution, and oxidised by aqua regia; after which, the tellurium is reduced, in the manner above described, by sulphite of ammonia.

Separation from Gold and other Metals by Chlorine.—Tellurium, when combined with reguline metals, can, in many cases, be very well separated by chlorine gas. A weighed quantity of the compound is exposed to heat, and to the simultaneous action of chlorine gas, in an apparatus similar to that represented at page 77. Chloride of tellurium is then volatilized, while the compounds of the chlorine with the other metals remain behind, if not of a volatile nature. The chloride of tellurium is led into a flask containing very dilute muriatic acid, wherein the chloride of tellurium dissolves, without producing a milky solution. The tellurium is reduced by sulphite of ammonia. By this process, tellurium can be separated from gold, with which it occurs in a native compound.

Separation from Tin, Antimony, and Arsenic.—The best method of quantitatively separating tellurium from tin, antimony, and especially from arsenic, has not yet been properly determined. According to BERZELIUS (POGGENDORFF'S Annalen, B. VIII. p. 413), arsenic, whether it be combined in the reguline state with tellurium, or as sulphuret of arsenic with sulphuret of tellurium, can be separated by mere distillation. Reguline tellurium then remains behind, because the sulphuret of tellurium also loses its sulphur in the heat. By this operation, however, a little of the tellurium can easily be volatilized with the other substances.

XXXIX. SELENIUM.

Reduction of Selenious Acid by Sulphite of Ammonia.—When selenium is contained in solution as selenious acid, the best way to estimate its quantity is by means of sulphurous acid: the method of operating is the same as with tellurium. The solution which contains the selenious acid is acidulated by muriatic acid, and acted on by a solution of sulphite of ammonia. The selenium is thereupon, in most cases, immediately reduced, and separates in the form of a cinnabar red powder, which remains a very long time suspended in the solution. But, if the solution be made to boil, the reduced selenium conglobes to a very small bulk, and becomes black. If, now, the addition of a fresh portion of sulphite of ammonia produces no red colour in the solution, the reduced selenium is gathered upon a weighed filter, and washed. It is then dried with the utmost degree of care, and when it loses no more weight by drying, its weight is finally determined.—Selenium, however, is often more slowly reduced by sulphurous acid. It is best, in all cases, after the reduced selenium has separated, to mix the liquid with a fresh quantity of sulphite of ammonia, to allow it to repose for some time, and then to boil it again. If no more selenium is then precipitated, the operator can be sure that the whole quantity has been reduced by the previous operation.

If the solution in which the selenious acid is to be reduced, contains nitric acid, the latter must be completely destroyed by muriatic acid, before the sulphite of ammonia is added. To this end, the solution is placed on the sand-bath, and muriatic acid is gradually added to the hot solution, as long as chlorine is disengaged. When the nitric acid has thus been entirely expelled, the selenium can be precipitated by sulphite of ammonia.

Quantitative Estimation of Selenic Acid.—When, however, the selenium is contained in a solution as selenic acid, it is impossible, according to **MITSCHERLICH** (**POGGENDORFF's** Annalen, B. IX. p. 630), to effect its reduction by sulphurous acid. The solution must then be kept boiling with muriatic acid, till it ceases to give out chlorine. The selenic acid is reduced by the muriatic acid to selenious acid, which can be reduced to selenium by sulphurous acid or sulphite of ammonia; a solution of either of the latter being gradually added to the acid solution.—As it is difficult, however, to reduce the last traces of selenic acid to selenious acid by muriatic acid, it is better to effect the estimation of selenic acid by precipitating it with a solution of nitrate of barytes. The substance thus precipitated is seleniate of barytes, which is as insoluble in diluted free acids as sulphate of barytes. When, therefore, a solution contains a seleniate, it should be acidulated by nitric acid, and acted on by a solution of nitrate of barytes. The resulting seleniate of barytes, like the sulphate of barytes, must be ignited. It is afterwards weighed; and the quantity of the selenic acid is calculated from the weight of the seleniate.

Precipitation of Selenious Acid by Sulphuretted Hydrogen Gas: Separation of Selenious Acid from the Earths and Alcalies, and from the Oxides of Manganese, Iron, Zinc, Cobalt, Nickel, &c.—The selenious acid is precipitated from acid solutions by sulphuretted hydrogen gas, affording a yellow-coloured sulphuret of selenium. When, therefore, selenium is contained in a solution as selenious acid, it can be very easily separated by sulphuretted hydrogen gas, from the alcalies and earths, and from the oxides of manganese, iron, zinc, cobalt, nickel, &c. The precipitated sulphuret of selenium is taken from the filter, while still wet, and treated with aqua regia: it must be digested therewith, until the selenium is completely dissolved, and only an extremely small portion of sulphur remains undissolved. It is better, however, to effect an entire solution by means of fuming nitric acid; for, it is possible for the undissolved sulphur to retain a portion of selenium. The solution must afterwards be digested with muriatic acid, till the nitric acid is completely destroyed. It must then be diluted with a little water, and treated with sulphite of ammonia, to occasion the reduction of the selenium.—But, as the bases above-named are not reducible by sulphurous acid, it is often a better plan to precipitate the selenium from the acid solution by sulphite of ammonia, instead of by sulphuretted hydrogen gas, and then to estimate the other substances in the filtered solution.—When the substances are combined in the reguline state with selenium, the compound is dissolved in heated nitric acid or aqua regia. The metals are much earlier oxidised than the selenium; but, after a long digestion, the latter likewise dissolves completely. Before the sulphite of ammonia is added to the solution, the nitric acid must be destroyed by muriatic acid.

Separation of Selenic Acid from the Alcalies and Earths, and from the Oxides of Manganese, Iron, Zinc, Cobalt, Nickel, &c.—When, instead of selenious acid, it is, on the contrary, selenic acid which is combined with the alcalies, earths, and above-named metallic oxides, then the separation of the selenium can be effected, neither by sulphurous acid, nor by sulphuretted hydrogen gas; since both of these reagents are without action on selenic acid. In that case, the solution must either be boiled with muriatic acid, till the selenic acid is reduced to selenious acid; or, what is better, the selenic acid must be directly precipitated by a solution of nitrate of barytes. The quantity of the selenic acid is reckoned from the weight of the precipitated seleniate of barytes.—When the seleniate to be analysed is insoluble, both in acids and water, such as, for example, the seleniate of barytes, it must be treated with muriatic acid, when boiled with which, the selenic acid is reduced to selenious acid. As the selenites which are insoluble in water, are soluble in acids, the reduction of the insoluble arseniate to arsenite is completely effected when the compound has dissolved in the muriatic acid.

Separation from Cadmium, Lead, Bismuth, Copper, Silver, Mercury, Manganese, Iron, Zinc, and Cobalt, by Bihydrosulphuret of Ammonia.—If the compound for analysis contains selenium in combination with metals whose oxides are precipitable from acid solutions by sulphuretted hydrogen gas, the separation may be effected by the following process: Metals of this description are,—cadmium, lead, bismuth, copper, silver, and mercury. The compound is dissolved in nitric acid or aqua regia; the solution is supersaturated with ammonia, and then acted on by bihydrosulphuret of ammonia; thereupon, the sulphuret of selenium dissolves, while the sulphurets of the other metals are precipitated. This method of separating selenium from the above-named metals is, in most cases, preferable to that by means of sulphurous acid; because, several of the oxides of these metals are, as well as selenious acid, capable of being reduced by sulphurous acid. When the selenium is combined with lead, with which it frequently occurs in nature, the compound can be analysed by no other means than by bihydrosulphuret of ammonia. For, if the protoxide of lead be precipitated from the solution of the seleniuret of lead in nitric acid, by the addition of carbonate of ammonia, the precipitate always contains a portion of selenious acid, even when a large excess of the precipitant has been applied. And when the protoxide of lead is precipitated from a similar solution by sulphuric acid, it is necessary, if the operator wishes to obtain the entire quantity of the sulphate of lead, to evaporate the solution to dryness, and to expose the dry mass to heat, until the free acid, both selenious and sulphuric acid, has been completely driven away. By operating in that manner, therefore, the quantity of the selenium cannot be determined. It is, likewise, impossible to precipitate the selenium by adding sulphurous acid to the solution of seleniuret of lead in aqua regia; because, although a portion of reduced selenium is thrown down, yet it is accompanied by selenite of lead and sulphate of lead, so that its estimation in this manner cannot be effected.

In the analysis of seleniuret of lead by bihydrosulphuret of ammonia, the operator proceeds in the same manner as in the separation of antimony and arsenic from that metal. The detailed description of this operation may be seen at pages 181 and 203. Although the sulphuret of selenium easily dissolves in bihydrosulphuret of ammonia, it is, nevertheless, proper, after having supersaturated the solution with ammonia, to add an excess of the bihydrosulphuret of ammonia, and to allow the whole to digest with heat for a considerable time. The undissolved metallic sulphuret is then filtered, and washed with water mixed with bihydrosulphuret of ammonia. The quantity of lead contained in the sulphuret is determined by the methods which have been already described.—The solution of selenium in bihydrosulphuret of ammonia is acidulated by muriatic acid, whereupon the sulphuret of selenium precipitates. The solution is warmed until it no longer smells of sulphuretted hydrogen gas, upon which the sulphuret of selenium is filtered. The precipitate, while still moist, is oxidised by aqua regia, and the selenium is reduced by sulphite of ammonia, in the manner described above.—When mercury is separated from selenium by this process, the solution containing the sulphuret of selenium must not be filtered from the sulphuret of mercury till the whole has become completely cold.—Manganese, iron, zinc, and cobalt, can also be separated from selenium by the operation here described.

Separation of Selenic Acid from Metallic Oxides.—When the metallic oxides which are precipitable from acid solutions by sulphuretted hydrogen gas, are, on the contrary, combined with selenic acid, their analysis may be proceeded in as follows: The compound for examination must be dissolved in water, if it be soluble therein, and the solution obtained be submitted to the action of a solution of nitrate of barytes, which produces a precipitate of seleniate of barytes. But it is also possible to precipitate the metallic oxides in the state of metallic sulphurets, by sulphuretted hydrogen gas, since this gas does not convert the selenic acid into sulphuret of selenium; the selenic acid, therefore, remains dissolved, and can be estimated in the solution filtered from the insoluble sulphurets. The latter method is particularly proper to be employed in the analysis of such seleniates as are insoluble in water, and which have bases which can be converted into metallic sulphurets by sulphuretted hydrogen gas: the seleniate of lead, for example, is a substance of this description. When this compound is to be analysed, it is mingled with water, and a current of sulphuretted hydrogen gas is passed through the mixture as long as it continues to be absorbed. The liquor is then filtered: the sulphuret of lead remains on the filter; the selenic acid is dissolved in the filtered solution.

Separation of Selenium from Metals by Chlorine.—The separation of selenium from metals can also be extremely well effected, by leading chlorine gas over the compound, and distilling by heat the volatile chloride of selenium from the fixed metallic chlorides. The seleniurets are much better, and in far shorter time, decomposed by chlorine gas than the antimoniurets and arseniurets. This method of analysing the seleniurets is, therefore, much to be recommended. The apparatus employed for this purpose, is such as is represented at page 77. It is proper that the glass tube soldered to the glass bulb *e*, and bent at a right angle, be not of too small a diameter.—A weighed portion of the seleniuret is placed in the bulb *e*; and when the apparatus is placed together, and is full of chlorine gas, the seleniuret in the bulb is heated by the smallest flame which can be produced by the spirit lamp with double current of air. The chloride of selenium immediately begins to volatilize. At first an orange-yellow oily liquid appears, which is the protochloride of selenium. This runs down the tube into the flask *k*, one-third of the capacity of which is filled with water. The protochloride of selenium is decomposed by the water, and selenium is precipitated. The chlorine which afterwards passes into the solution redissolves the greater part of the precipitated selenium; yet, a small portion of the selenium often remains in little lumps at the bottom of the flask. Subsequently, it is only the perchloride of selenium which is produced. This condenses in the bent glass tube; and if the tube be of too small a diameter, is liable to stop it. It is, of course, necessary to drive the sublimed perchloride of selenium very frequently towards the flask, by applying to the tube the flame of a small spirit lamp.—The seleniurets are so easily decomposed by chlorine gas, that all the selenium contained in a portion of the compound of some grammes[*] in weight, is completely converted into chloride of selenium in the course of an hour. When the perchloride of selenium has been driven as far as possible from the glass bulb by means of the flame of a small spirit lamp, and no new perchloride of selenium can be seen to pass from the bulb into the tube, the operation is ended. The bulb is then allowed to cool gradually; when it is cold, that part of the tube in which a portion of perchloride of selenium still remains, is cut off with a sharp file, and allowed to drop into the flask *k*, which must be instantly closed.—The metallic chlorides which remain in the bulb are to be subsequently analysed after methods which have been already described. When lead alone was combined with the selenium, it is sufficient to weigh the glass bulb, first with the chloride of lead within it, and afterwards by itself, whereby the quantity of the chloride of lead is readily ascertained. But when copper is present, it is useless to ascertain the weight of the chlorides. If the compound contained iron, a portion of perchloride of iron will be found with the fixed chlorides, but another portion will have been sublimed with the perchloride of selenium.

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[*] A gramme is equal to 15·438 grains Troy.

The solution in the flask *k* is exposed to heat, to volatilize the free chlorine. Muriatic acid is then added, and the selenium is precipitated by sulphite of ammonia. Notwithstanding the readiness with which the precipitation of selenium is effected by sulphurous acid in solutions of selenious acid, yet this precipitation is effected with just as much difficulty, when a solution of perchloride of selenium in water, has been exposed for a long time to the action of a current of chlorine. Upon adding sulphurous acid to a solution of selenious acid, a cinnabar-red colour is produced in a few moments; but, upon adding sulphurous acid to the solution of perchloride of selenium, it is very common to obtain no precipitate whatever. It must be inferred from this fact, that selenic acid has been produced. It is only by a long continued boiling with muriatic acid, that the solution can be brought into such a state as to admit of the complete reduction of the selenium it contains, by sulphite of ammonia. The liquid filtered from the reduced selenium must be preserved for a considerable time, then boiled afresh with muriatic acid, and again acted upon by sulphite of ammonia: the object of this second process is to ascertain whether all the selenium has been reduced by the first. When the seleniuret contained iron, the quantity of the perchloride of iron which distilled over with the perchloride of selenium, must be estimated in the liquid filtered from the precipitated selenium.

Separation from the Oxides of Tellurium, Arsenic, Antimony, and Tin.—There are certain metals which can be precipitated from acid solutions by sulphuretted hydrogen gas, but afford sulphurets that are soluble in bihydrosulphuret of ammonia. The separation of selenium from such metals as these, might be effected by converting the selenium into selenic acid, which remains unaltered by sulphuretted hydrogen gas, but admits of the precipitation of the accompanying metals. MAGNUS (Inaugural Dissertation: *de Tellurio,* p. 12) has proposed the following operation for separating selenium from tellurium and arsenic: The compound is melted with nitrate of potash, in a small porcelain capsule over the spirit lamp with double current of air; the result afforded by this operation is a mixture of oxide of tellurium combined with potash, with arseniate of potash, and seleniate of potash. The melted mass, after being dissolved in water, could be acidulated by an acid, which, however, must not be muriatic acid, and then be subjected to the action of a current of sulphuretted hydrogen gas; by this means, the tellurium and arsenic would be separated by precipitation from the selenium.

Separation of Selenic Acid from Selenious Acid.—The respective quantities of selenic acid and selenious acid, when both occur in the same solution, can be very easily estimated. The quantity of the selenious acid is first determined, by operating either with sulphuretted hydrogen gas or sulphurous acid; after which, the selenic acid is estimated as seleniate of barytes, or it can, instead, be reduced to selenious acid by the action of muriatic acid.

XL. SULPHUR.

Quantitative Estimation of Sulphur.—The quantitative determination of sulphur can be effected with the greatest accuracy: the operator converts the sulphur into sulphuric acid, precipitates the acid by a salt of barytes, and reckons the quantity of sulphur from the weight of the sulphate of barytes. To this end, the sulphuret is commonly digested with nitric acid or aqua regia: it then becomes oxidised, and is dissolved in the acid. The sulphur is converted by the excess of acid into sulphuric acid, and never into any lower oxide of sulphur. The complete conversion of the sulphur into sulphuric acid requires, however, a large quantity of acid, and a very long digestion, assisted by heat. In almost all cases, the metal which is combined with the sulphur is oxidised much sooner than the sulphur itself; the whole quantity of the resulting metallic oxide is generally dissolved, while the greater part of the sulphur is still undissolved. The latter exhibits itself, after a long digestion, in the form of hard, yellow lumps; and often, after a short digestion, lies upon the bottom of the vessel in the state of a yellow powder. Since the perfect oxidation of the sulphur requires too long a time, the process is arrested when the sulphur, known by its peculiar yellow colour, is separated; the solution is then diluted with water, and filtered through an accurately weighed filter. Thereupon the sulphur is washed and dried at a very moderate degree of heat, until it ceases to lose weight. The sulphuric acid, which is produced by the digestion, is precipitated from the filtered solution by a solution of chloride of barium. The operator calculates from the weight of the sulphate of barytes, the quantity of sulphur which it contains. The sum of the two portions of sulphur thus found, gives the quantity of sulphur in the substance under examination.

When a substance containing sulphur is oxidised by fuming nitric acid, the action is much more violent than when, for this purpose, a weaker acid or aqua regia is employed. If the sulphuret be pulverised, and then treated with a sufficient excess of fuming nitric acid, no sulphur is commonly separated, but the whole quantity of it is converted into sulphuric acid. In general, however, the fuming nitric acid is not employed, since its use requires the taking of too many precautions. That none of the compound may, upon being treated with fuming nitric acid, be projected from the vessel and lost, it is best to place it in a matrass, and to pour the fuming acid upon it, in small portions, through a funnel. The operator durst not, in this operation, add a new quantity of the acid, until the working produced by the previous addition is totally at an end. A large quantity of water is afterwards added to the oxidised mass, and when the whole of the sulphur is dissolved, the sulphuric acid which has been produced, is precipitated by a solution of chloride of barium.

The sulphate of barytes which is obtained by these operations, is much more difficult of being washed clean than is generally the case, because the coexistence of nitric acid and of an excess of the salt of barytes, in the solution, occasions the simultaneous precipitation of a portion of nitrate of barytes, which is only to be separated from the sulphate of barytes by washing with hot water.

The farther progress of the analysis, in the general examinations of sulphurets, is extremely simple: the operator has only to determine the quantity of the oxides held in solution by the aqua regia or nitric acid, which is filtered from the sulphate of barytes. But as the excess of barytes employed to effect the full precipitation of the sulphuric acid might produce errors, it is best, in the first place, to separate this earth from the solution. For this purpose, sulphuric acid is added to the solution, care being taken to avoid adding a great excess. The operator separates the sulphate of barytes by filtration, washes it clean, and throws it away. The washing of this portion of sulphate of barytes is effected with ease. The oxides contained in the solution can then be precipitated.

Separation from Manganese, Iron, Zinc, Cobalt, Nickel, Cadmium, and Copper.—It is possible to analyse, after this method, the greater part of the different compounds of sulphur with metals. The compounds of sulphur with manganese, iron, zinc, cobalt, nickel, cadmium, and copper, can, for example, be all treated in this manner; yet many of these compounds, especially those of sulphur with manganese, and some of those of sulphur with iron, require particular management: the operator must employ nitric acid which is pretty strong, and, where it is possible, hot; or, instead of that, must use strong and hot aqua regia. If he employ a very weak acid, and neglect to assist its action by heat, a slight disengagement of sulphuretted hydrogen gas may easily take place, and thus occasion a loss of sulphur. It is better also to pulverise these compounds, and not to operate upon them in large pieces; because the latter become oxidised at the surface, and acquire a coating of sulphur, which often protects a portion of the compound from the action of the acid. The sulphur which is separated in these analyses has generally at first a grey colour. The operator must not filter the solution, until, by continuing the digestion, the sulphur has been rendered quite yellow. When the weight of the sulphur has been determined, after having been dried completely upon the weighed filter, it must be burned, that the operator may ascertain whether it be pure or not. For this purpose, the operator takes from the filter as much sulphur as he is able to separate, and exposes it to heat in a small counterpoised porcelain crucible, upon which it burns and volatilizes. If it give a fixed remainder, he determines its weight: the remainder consists in general of an oxide of the metal with which the sulphur had been combined. This oxide was naturally contained as metallic sulphuret in the separated sulphur; but was, on being heated in contact with the air, converted into basic sulphate. This basic sulphate being generally in but very small quantity, lost its sulphuric acid on the continuance and increase of the heat, and became converted into oxide. This is generally the case. From the weight of the remaining oxide, the operator calculates the quantity of metal which it contains; he subtracts this weight from that of the sulphur, and thus finds the true quantity of the sulphur contained in the original compound. He then dissolves the oxide in muriatic acid, upon which a small quantity of matrix or sometimes of silica remains behind, the weight of which is estimated in the usual manner. These insoluble remainders are met with, not only in the sulphurets which are found in nature, but also in those which are prepared by chemists. The solution of the small portion of oxide is tested with a solution of a salt of barytes, to determine whether the ignited remainder contained any sulphuric acid. If sulphate of barytes is produced, the quantity of sulphuric acid which it contains is calculated, and deducted from the estimated quantity of the oxide. The quantity of sulphur contained in this small quantity of sulphuric acid being then determined, is added to the previously-estimated weight of the sulphur.—When the quantity of the ignited oxide is very small, and a very strong heat has been employed in the ignition, it is not usual to find it to contain sulphuric acid. When the quantity of the remaining oxide is greater, when, for example, it exceeds the third of a grain, it is a proof that the separated and weighed sulphur was not of a pure yellow colour, and had not undergone a sufficiently long digestion.

Separation from Lead.—The analysis of other sulphurets is affected by a somewhat different mode of treatment. The compound of lead and sulphur must be pulverised, converted by fuming nitric acid into sulphate of lead, and treated in the manner which has been detailed at page 101. When, however, it is desirable to determine with exactness the quantity of sulphur contained in a compound of lead and sulphur, the best method of proceeding is to treat the compound with gaseous chlorine, which is a process that will be described in a subsequent part of this section.

Separation from Bismuth.—The compound of sulphur and bismuth must be decomposed by pure nitric acid, and not by aqua regia. The precipitated sulphur must be washed with water acidulated by a little nitric acid, and the washing must be continued until the whole of the oxide of bismuth is separated. The oxide of bismuth is afterwards precipitated from the filtered solution by carbonate of ammonia. The solution is then filtered from the precipitate, rendered acid by muriatic acid, and mixed with a solution of chloride of barium to precipitate the sulphuric acid.

Separation from Silver.—The compounds of sulphur and silver must also be decomposed, solely by pure nitric acid. From the solution which is filtered from the sulphur, the silver is precipitated by muriatic acid; and from the solution which is filtered from the chloride of silver, the sulphuric acid is precipitated by chloride of barium.

Separation from Mercury.—The compounds of sulphur with mercury can be treated only with aqua regia, as nitric acid, used alone, has not the power of decomposing them. Hereby, the sulphur is very often completely oxidised. The sulphuric acid is first precipitated by chloride of barium, and then the quantity of the mercury is determined. This determination, however, is attended with difficulties on account of the presence of the nitric acid. The best way of proceeding is to precipitate the mercury by a current of sulphuretted hydrogen gas, a process which has been already described at page 123.

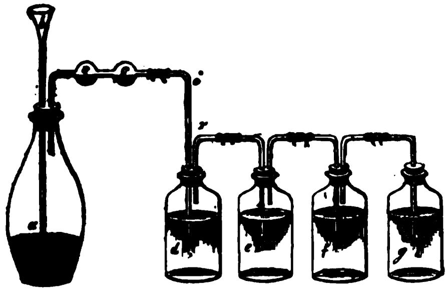
Separation from Gold and Platinum.—From the compounds of sulphur with gold and platinum, the sulphur is expelled by ignition; the metal remains behind in a pure state, and can be weighed. The quantity of the sulphur is ascertained from the loss of weight.

Separation from Tin.—The compounds of sulphur with tin can be oxidised by aqua regia. It is better, however, to decompose them by gaseous chlorine, according to the method which will be described farther on.

Separation from Titanium.—The compound of sulphur with titanium is converted into titanic acid by strong ignition in the atmosphere, and from the weight of the titanic acid, the composition of the sulphuret is calculated, supposing the latter to have been pure. If, however, the operator desires to determine, by a direct experiment, the quantity of sulphur in this compound, it is best to oxidise it with fuming nitric acid, so as to convert all the sulphur into sulphuric acid. The solution is diluted with water, and the titanic acid is precipitated by ammonia. The solution is filtered, and acidulated by muriatic acid, and the sulphuric acid is precipitated by chloride of barium.—The compound can also be decomposed by chlorine gas, as will be shown farther on.

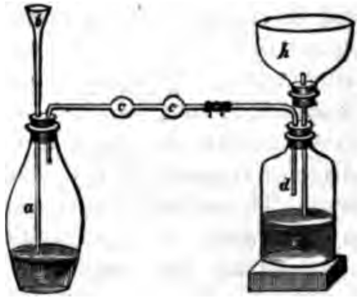
Separation from Antimony, Arsenic, Tellurium, Selenium, &c.—The compounds of sulphur with antimony, arsenic, tellurium, selenium, and other metals, are examined after methods which have been already described in the sections wherein these metals were the subjects under consideration.

Separation from the Metals of the Alcalies and Earths.—The compounds of sulphur with the metals of the alcalies and alcaline earths, are difficult of examination; because, upon being treated by acids, even by those which are best adapted for oxidising, they disengage sulphuretted hydrogen gas. It happens very seldom that they can be oxidised by fuming nitric acid, in such a manner as to avoid a loss; for even this acid often occasions the disengagement of a small portion of sulphuretted hydrogen gas. The best general process is to decompose their solutions by an acid; the oxide of the alcaline metals then combines with the acid which is employed, and its quantity can be determined by methods which have been already described. The quantity of sulphur is ascertained, in this operation, from the loss of weight. If, however, the operator should desire to determine directly the quantity of sulphur, he can effect the object by ascertaining the volume of the sulphuretted hydrogen gas, disengaged during the action of an acid upon the alcaline sulphuret. This is the method which is generally followed; but it is better to lead the sulphuretted hydrogen gas through a metallic solution, and to determine the quantity of sulphur contained in the resulting metallic sulphuret. The method of proceeding in this operation, is as follows: The solution of the weighed metallic sulphuret, or the dry compound of sulphur with the metal of an alcali or an alcaline earth, is put into a flask *a*. This flask is closed air-tight with a cork, through which, as in the case of a common flask for the preparation of gases, there passes the neck of a funnel *b*, which reaches nearly to the bottom of the flask: there is moreover a glass tube for the conveyance of the gas passed through the cork. This glass tube is connected by means of a tube of Indian rubber with another glass tube, marked *i*. The glass tube *i* passes through the cork with which the flask *d* is closed air-tight, and goes an inch below the surface of the solution it contains. Another tube *r* passes through the same cork. The flask *d* is filled to two-thirds of its capacity with a metallic solution. The tube *r* is placed about half an inch above the surface of the solution, and on the outside of the flask is bent at a right angle. The four flasks, *d*, *e*, *f*, and *g*, are connected with one another in the same manner. The cork which closes the flask *g* must not fit it air-tight like the others, but only be placed in the flask loosely. For the metallic solution, with which the flasks are to be filled to two-thirds of their capacity, the operator may choose a solution of acetate of lead: in this case, he calculates from the weight of the resulting dry sulphuret of lead, the quantity of the decomposed sulphuretted hydrogen gas. It is better, however, to fill the flasks with a solution of chloride of copper. In the first three flasks, *d*, *e*, and *f*, it is proper to pour a neutral solution of chloride of copper, but in the fourth flask *g* a solution of chloride of copper rendered alcaline by caustic ammonia, the sulphuretted hydrogen gas being absorbed much better and quicker by such a solution than by a neutral solution of chloride of copper.—If the operator should not have employed a solution of the metallic sulphuret for decomposition, he must pour so much water into the flask *a*, that the neck of the funnel *b* may be deep under the surface of the solution. He then cautiously



pours the acid, which is to effect the decomposition of the metallic sulphuret, in small quantities through the funnel *b*. Diluted sulphuric or muriatic acid is generally employed for this purpose. There is now a disengagement of sulphuretted hydrogen gas, which is absorbed by the solutions in the flasks, and occasions a deposition of sulphuret of copper to take place. Particular care must be taken to produce a very slow disengagement of gas; for if too rapid a current passed through the apparatus, it would be very possible for a portion of it to escape absorption, and to pass out of the vessels. A slow disengagement of gas is effected by a very cautious addition of the acid. It is necessary that the glass tubes which pass into the metallic solutions, do not end very deep under the surface of the liquid. When the disengagement of sulphuretted hydrogen gas has quite ceased, the upper part of the flask *a* is still full of this gas, while the acid retains a portion of it in solution. That as little as possible of the gas may remain dissolved in the liquid, the operator adds to the sulphuret which is to be decomposed only a very small quantity of water. But when the disengagement of the gas has quite ceased, it is proper to adopt the following method of expelling the sulphuretted hydrogen completely from the flask. The operator makes the solution in the flask very strongly acid; he then carefully heats the mixture, and afterwards, when it has become cold, carefully and gradually pours through the funnel *b*, a concentrated solution of carbonate of ammonia. Hereupon there is a disengagement of carbonic acid gas, which drives all the sulphuretted hydrogen gas into the other flask, and occasions a perfect absorption. The parts of the apparatus are then separated. The sulphuret of copper which has been produced, is filtered as quickly as possible. It is not necessary to wash it; but it must be oxidised, and the resulting sulphuric acid must be precipitated by a salt of barytes. From the weight of the sulphate of barytes so obtained, the quantity of sulphur contained in the substance submitted to examination, is calculated. That the whole of the sulphur in the sulphuret of copper may be fully oxidised, it is best to effect the oxidation by fuming nitric acid. If it should be desirable to avoid the use of fuming acid, and to employ common nitric acid or aqua regia, the sulphuret of copper must be oxidised without the filter, in order that the quantity of precipitated sulphur may be determined: this, however, it is not easy to do.—A solution of sulphate of copper is cheaper than a solution of chloride of copper, yet it cannot be employed in this experiment. The sulphuret of copper thrown down from a solution of sulphate of copper would require to be well washed; but during the washing, a portion of it might become oxidised. This would more especially be the case when the sulphuret of copper was to be separated from a solution which had previously been made alcaline by ammonia.—Should a solution of acetate of lead be employed, it must not be rendered ammoniacal, or the weighing of the sulphuret of lead, and the subsequent calculation of the quantity of the sulphur, will not be possible.

This method of estimating the quantity of sulphur in a substance, by converting it into sulphuretted hydrogen gas, is particularly worthy of adoption, in the cases where the sulphuretted hydrogen gas is accompanied by other gases incapable of being absorbed by the metallic solution, or at any rate by the metallic solution contained in the first three flasks, *d*, *e*, and *f*. Gases of this description are hydrogen and carbonic acid. When, on the other hand, the operator is certain that the decomposition of the substance will occasion the evolution of no other gas than sulphuretted hydrogen, he can make use of an apparatus which is much less complicated. The flask *a*, in which the production of the gas is effected, is constructed precisely as in the foregoing apparatus. A funnel *b*, with a long neck, passes likewise through the cork with which the flask is closed air-tight, and nearly touches the bottom of the vessel. The cork is also traversed by a glass tube, which is connected by an Indian rubber tube with another glass tube *d*. This is also bent at a right angle, and passes through the cork into the flask *e*, which is half filled with a metallic solution, and closed air-tight. The tube *d*, however, does not dip into the liquid, but ends



about an inch above its surface. Besides these, there passes another and straight glass tube through the cork of the flask *e*, the one end being near the bottom of the flask, the other proceeding pretty far above the cork. At the upper end of this tube a flask *h*, without a bottom, is fixed by means of a cork. A large medicine phial with the bottom cut off, may be employed for this purpose. The straight tube must pass through the cork a little way into the flask *h*. The joinings must all be air-tight. When the apparatus is fitted together, diluted sulphuric acid, or muriatic acid, is cautiously poured through the funnel into the vessel where the decomposition of the sulphuret is to be effected; thereupon, an evolution of sulphuretted hydrogen gas takes place. This gas, passing into the flask *e*, forces the metallic solution to rise into the vessel *h*. By the pressure which is produced by the liquid in the vessel *h*, the absorption of the sulphuretted hydrogen gas by the metallic solution in the flask *e*, is much facilitated. When no more gas is disengaged upon the addition of fresh acid, the acid solution in the flask *a* is gradually heated. It is then allowed to cool, and a solution of carbonate of ammonia is cautiously poured through the funnel *b*; this produces a disengagement of carbonic acid gas, which expels from the flask *a* all the sulphuretted hydrogen gas that may have remained there.—The best metallic solution to put into the flask *e* is a solution of chloride of copper, with excess of ammonia. This not only serves to absorb the sulphuretted hydrogen gas, but saturates the carbonic acid, which is subsequently generated. When all the sulphuretted hydrogen gas is absorbed, and the solution has returned from the vessel *h* into the flask *e*, the apparatus is carefully disjointed. The metallic sulphuret contained in the flask, is then treated in the manner which has been described above.

In these operations, in which a metallic sulphuret has been decomposed, there still remains to be determined the quantity of oxide dissolved by the acid poured into the gas flask *a*. Besides this, however, the decomposition of the sulphuret may have been accompanied by the deposition of a portion of pure sulphur. This is always the case, when the sulphuret which is decomposed contains a greater number of atoms of sulphur than the oxide which is produced contains atoms of oxygen. Great care must then be taken that the solution in the flask *a* is always acid, even after the addition of the carbonate of ammonia. The sulphur thus separated must be filtered upon a weighed filter, then dried and weighed. The quantity of the oxide can then be determined. The solution is generally evaporated to dryness and is ignited. When the ammoniacal salts have thus been expelled, the remainder consists of the metallic oxide, combined with the acid which was employed to decompose the sulphuret; or when muriatic acid has been used for this purpose, the fixed remainder consists of the metal which was originally combined with sulphur, now combined with chlorine. When the operator possesses a large quantity of the metallic sulphuret which is to be examined, it is best to weigh and decompose a separate portion, with a view to the estimation of the oxide. When this is done, it is unnecessary, in the analysis undertaken to determine the quantity of sulphur, to disengage carbonic acid gas from carbonate of ammonia; since carbonate of potash can be employed for that purpose.—When the metallic sulphuret for examination cannot be weighed without difficulty, an indeterminate portion of it may be decomposed. The composition can be found from the relation which the quantity of oxide produced, bears to the quantity of sulphur.

Separation from Metals by Chlorine Gas.—The compounds of sulphur with most metals can also be analysed in the following manner: A weighed portion of the compound for examination, is heated in the apparatus depicted at page 77, and gaseous chlorine is passed over it while hot. Chloride of sulphur is formed and sublimed, while, in most cases, the metal operated upon, combines with chlorine and remains behind. The chloride of sulphur is treated in the manner which has already been described, when speaking of the mode of treating the volatile chlorides, that is to say, it is conducted into a flask one-fourth part filled with water. It is proper to be cautious in these analyses, and not to allow the chlorine to pass through the apparatus too rapidly. The chloride of sulphur is decomposed by the water, and gives birth to sulphur and sulphurous acid, and the latter, when in contact with the moist chlorine gas which fills the upper part of the flask, is converted into sulphuric acid. With a view to ensure the entire conversion of the sulphurous acid into sulphuric acid, the operator must take the precaution of not warming the substance to be examined, until the whole apparatus, including the flask which constitutes the receiver, is filled with chlorine gas; a state of things which the green colour of chlorine gas renders easy of observance. The heating of the sulphuret requires only the smallest flame which can be produced by a spirit lamp with circular wick. The sulphur resulting from the decomposition of the chloride of sulphur forms drops which remain long in a fluid state. Besides the chloride of sulphur, the volatile chlorides of metals also distil over; the metallic chlorides which are not volatile remain behind in the bulb. The volatile metallic chlorides, and the chloride of sulphur are driven by the flame of a small spirit lamp continually towards the flask containing the water which is to dissolve and decompose them. When the volatile chlorides cease to be formed, and expelled from the glass bulb, the operation is ended. The operator then gradually reduces the heat applied to the glass bulb, and, when the whole is quite cold, disjoins the apparatus. The volatile metallic chlorides must have been previously driven so far from the bulb, that the glass tube is as free as possible from them as far as *h* (see the figure at page 77). At this point the tube is cut with a sharp file, and the under part is permitted to fall into the vessel *k*. But at this instant the vessel must be closed with a good-shutting glass stopple, because the chlorides in the under part of the glass tube are suddenly decomposed by the water in the flask *k*, which produces such a degree of heat, that a portion of the volatile substance escapes in vapour before the water has a sufficient opportunity of acting upon it. This is particularly the case, when much chloride of sulphur is contained in the tube. If small portions of the volatile chlorides still remain in the part of the conducting tube which is not cut off, the tube must be cut again, the chlorides must be washed out with water, and the solution be added to that contained in the flask *k*. Thereupon, in order to determine the weight of the metallic chlorides which are not volatile, the operator weighs the glass bulb with the chlorides contained in it; he then empties, cleans, and dries the glass bulb, and weighs it again. As the glass bulb with the tubes joined to each end was weighed alone, before the introduction of the compound for analysis, it is now only necessary to clean, dry, and weigh the pieces of glass tube which were cut off, to determine the weight of the fixed chlorides contained in the bulb. The weight of the glass first found, deducted from the common weight of the bulb, the chlorides and the pieces of tube, gives the weight of the chlorides. If the compound submitted to examination contained copper, the weighing of the fixed chlorides is of no use.

The analysis of the fixed metallic chlorides is effected by processes which have been fully explained in the preceding sections. They are first treated with muriatic acid and water, with access of atmospheric air. When copper is contained in the compound, the resulting protochloride of copper is, after some time, fully converted into perchloride of copper. If silver is present, it remains undissolved in the state of chloride of silver. When lead is present as well as silver, the chloride of lead which is produced, can be completely separated from the chloride of silver, by merely treating the mixture with water.

The liquid in the receiver holds the volatile metallic chlorides in solution; that is to say, when they are capable of dissolving therein. Besides these, it contains sulphuric acid and sulphur, and the estimation of the quantity of the latter substances is the first thing which must be attempted. If the operator allows the chlorine gas, after the complete decomposition of the substance submitted to analysis, to stream very slowly and during a very long time through the solution in the receiver, the consequence will be, that the sulphur which was at first precipitated will redissolve, and produce sulphuric acid. The complete conversion of the precipitated sulphur into sulphuric acid requires, however, a considerable time; often a whole day, sometimes several days. But although it requires a long time, the operation is not very troublesome; the operator has only to take care that the chlorine gas is, in the ordinary manner, very slowly, yet continually disengaged.

When the decomposition is finished, the receiver is exposed to an extremely moderate heat, until the free chlorine is expelled. If free sulphur be present in the solution, the operator must still wait some time before he proceeds with the filtration, because the sulphur not only remains a long time in the liquid state, but after the solution has been warmed, continues smeary for some time. When the sulphur has become hard, it is filtered upon a weighed filter, then dried and weighed. The sulphuric acid produced by the operation is precipitated from the filtered solution, by a solution of chloride of barium, or of some other salt of barytes, and the quantity of sulphur is calculated from the weight of the sulphate of barytes. The filtered solution still contains the metals, which, in the state of metallic chlorides, were distilled over with the chloride of sulphur. These metals still remain for estimation.

Separation from Antimony by Chlorine Gas.—When the compound to be examined contains sulphuret of antimony, and is to be decomposed by chlorine gas, the liquid in the flask, which serves for receiver, must consist of a weak solution of tartaric acid mingled with muriatic acid. After the decomposition, the sulphur is first separated, and the sulphuric acid is then precipitated by a salt of barytes.

The antimony is afterwards precipitated by a current of sulphuretted hydrogen gas. Before, however, this last operation is executed, it is advisable to separate the excess of barytes which may have been added to the solution. This is effected by sulphuric acid, of which considerable care should be taken to add no more than may be necessary. It remains to be observed hereby, that the sulphate of barytes, of which the quantity is to be estimated, ought to be filtered as soon as it has fully subsided; for, if the whole be allowed to remain several days unfiltered, a deposition of crystallized supertartrate of barytes takes place, notwithstanding the presence of muriatic acid, and from this substance the sulphate of barytes is freed, by washing, with considerable difficulty.

Separation from Antimony and Arsenic by Chlorine Gas.—If the substance to be examined contains both sulphuret of antimony and sulphuret of arsenic, the liquid in the receiver, must, as in the preceding case, be a solution of tartaric acid; but this is not necessary when sulphuret of arsenic alone is present.

Separation from Antimony and Iron by Chlorine Gas.—When the sulphurets which are to be decomposed by chlorine gas contain sulphuret of iron, a portion of the resulting perchloride of iron is volatilized during the operation. It is impossible, however, to drive over the whole of the iron in the state of perchloride, in company with the other volatile metallic chlorides and chloride of sulphur, since we dare not, in the decomposition of the metallic sulphurets, employ too high a temperature. Neither is it possible to manage the operation in such a manner as to make all the perchloride of iron remain with the fixed chlorides. The chlorine gas is therefore permitted to pass over the heated substance, until the perchloride of iron which distils over ceases to be accompanied by any other volatile chloride. The perchloride of iron is easily known by its colour, and by the crystalline spangles which it forms when it is driven onwards in the tube into which it has sublimed, by the application of the flame of a small spirit lamp. By these characters it is readily distinguishable from other more volatile chlorides, namely, from chloride of antimony, especially, as, by the decomposition by chlorine gas of the compounds of sulphur and antimony, only solid protochloride of antimony is formed, and not the fluid perchloride of antimony. When, now, the continuance of the operation occasions the volatilization of nothing but perchloride of iron, the apparatus is allowed to cool. The greater part of the perchloride of iron then remains in the glass bulb with the fixed chlorides; it is separated therefrom by the processes which have already been detailed. The far smaller portion of the perchloride of iron which has been distilled over with the volatile chlorides, is next to be separated. If the substance submitted to analysis contained antimony, and on this account, the receiver has been supplied with a liquor containing tartaric acid, it is proper to commence by precipitating the antimony by sulphuretted hydrogen gas; to filter the solution from the sulphuret of antimony, to supersaturate it with ammonia, and to precipitate the iron by bihydrosulphuret of ammonia. It is, in this case, impossible to estimate the quantity of iron in any other manner, on account of the presence of the tartaric acid. The sulphuret of iron thus obtained, must be converted into peroxide of iron by the method described at page 53.

Separation from Zinc by Chlorine Gas.—When the sulphuret which is decomposed by chlorine gas contains sulphuret of zinc, it is found that, when too strong a heat has not been employed to effect the decomposition, the whole of the chloride of zinc remains with the fixed metallic chlorides. It has been already observed, at page 95, that it is only the hydrated, and not the anhydrous chloride of zinc, which is easily volatile. When, however, too strong a heat has been applied in the decomposing process, a very small quantity of chloride of zinc will be found with the volatile chlorides, from which it must be separated according to the processes which have already been described. If antimony is contained in the substance submitted to examination, the zinc is precipitated as sulphuret of zinc, in company with the sulphuret of iron. The two sulphurets are then oxidised and separated.

Separation from Antimony, Silver, and Lead.—The employment of gaseous chlorine in the decomposition of metallic sulphurets is especially to be recommended when the substance submitted to examination contains a variety of metallic sulphurets. It is the only method which can be employed in the analysis of such sulphurets as contain, at the same time, sulphuret of antimony and other sulphurets, the metals of which constitute, with chlorine, compounds that are either insoluble in water and acids, or only soluble therein in a very slight degree. Such sulphurets, for example, are those of silver and lead, which frequently occur in nature, combined with sulphuret of antimony. The metals of these sulphurets can, it is true, be very well separated from one another by bihydrosulphuret of ammonia; but then, of course, the quantity of sulphur cannot be determined. If we attempt to oxidise these metals by aqua regia, we obtain a residue of insoluble chloride of silver, and difficultly soluble chloride of lead, mingled with the separated sulphur. If we treat them with nitric acid, we obtain a mixture of sulphur with oxide of antimony or antimonious acid. We could, indeed, completely oxidise the whole of the sulphur by fuming nitric acid; but, as this reagent does not fully precipitate the oxide of antimony, but permits a portion of it to remain in solution, it is evident, that the method of decomposing these sulphurets by gaseous chlorine, is preferable to all others.

Analysis of Sulphur Salts.—All metallic sulphurets are decomposable by gaseous chlorine, but the decomposition is not in all cases effected with the same facility. The compounds of sulphuret of antimony and of sulphuret of arsenic with basic metallic sulphurets—compounds belonging to those, to which BERZELIUS has given the name of *sulphur salts*—are remarkable for the easiness, the quickness, and the completeness with which they are decomposed. The use of chlorine gas is, therefore, particularly advisable when these substances have to be analysed, more especially when the sulphuret of antimony or the sulphuret of arsenic is combined with those sulphurets whose metals are capable of precipitation from acid solutions, which is almost always the case. When, however, sulphuret of antimony or sulphuret of arsenic is combined only with sulphurets of iron or of other metals which cannot be precipitated from acid solutions by sulphuretted hydrogen gas, it is better to effect the oxidation by aqua regia, than to treat the compound with chlorine gas. The operator then dissolves the metallic sulphurets in aqua regia; and if sulphuret of antimony be present, adds tartaric acid to the solution, at the same time taking care to dilute it properly with water. He filters the separated sulphur, and precipitates the sulphuric acid which has been formed, by a salt of barytes. He again filters the solution, precipitates the excess of the barytic salt by sulphuric acid, and then precipitates the antimony and the arsenic by sulphuretted hydrogen gas. He filters the solution from the sulphurets of antimony and arsenic, supersaturates it with ammonia, and precipitates the iron or the other metals which have escaped precipitation by the sulphuretted hydrogen gas applied to the acid solution, by bihydrosulphuret of ammonia now applied to the ammoniacal solution. On account of the presence of tartaric acid, no other precipitant can be employed for this purpose.—It is only when nickel is present, that the treatment of the compound with chlorine gas is to be preferred to that with aqua regia: the reason of this peculiar distinction is, that nickel is difficult of precipitation from neutral or ammoniacal solutions by bihydrosulphuret of ammonia.

The length of time occupied by the decomposition of metallic sulphurets by chlorine gas is different. The compounds of the sulphuret of antimony and the sulphuret of arsenic with basic metallic sulphurets, are completely decomposed in one hour from the time when, the whole apparatus being full of chlorine gas, the operator begins to heat the glass bulb; the quantity submitted to analysis being supposed to be a few grammes*. No part of the substance then remains undecomposed in company with the fixed metallic chlorides. Simple metallic sulphurets are not so easily decomposed. Still more tedious is the decomposition of compounds formed of metallic sulphurets with metallic arseniurets or metallic antimoniurets, such as arsenical cobalt (Glanzcobalt), nickel-glance (Nickelglanz), nickel-antimonial ore (Nickelspiesglanzerz). These compounds may be kept in quantities of only a very few grammes, continually heated and exposed to an incessant current of chlorine gas for twelve hours, or still longer, and yet not experience a complete decomposition.

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* A gramme is about 15½ English grains.

When the decomposition by chlorine has not been complete, the fixed chlorides remaining in the bulb must be dissolved in water, and the undecomposed substance separated by filtration. The weight of this portion is then determined, and deducted from the weight of the quantity submitted to analysis. If chloride of silver be contained among the fixed chlorides, it remains, of course, with the undecomposed substance. It might, indeed, be dissolved by ammonia, but as fused chloride of silver is difficult of solution in ammonia, the attempt to separate these substances in such a manner only renders the analysis more complicated. In this case, the decomposition by chlorine gas is consequently less worthy of recommendation.

The compounds of sulphurets of antimony and sulphuret of arsenic with basic metallic sulphurets, are completely decomposed by chlorine gas, even when employed in large pieces. It is, however, absolutely necessary to employ all the native sulphurets which are to be decomposed by chlorine gas, in the state of powder. One reason for recommending this precaution is, that nearly all large pieces of these substances, when first acted upon by heat, decrepitate, by which small portions could very easily be thrown out of the bulb, and might even pass into the vessel which serves for the receiver.—The other metallic sulphurets, which are difficult of decomposition, must never be employed but in a pulverized state.

Separation from Antimony, Bismuth, and Silver, by Hydrogen Gas.—A few, but only a very few, metallic sulphurets, are converted into reguline metals, when they are heated in an atmosphere of hydrogen gas. The composition of these sulphurets, can, consequently, be found by heating them in an apparatus similar to that depicted at page 83. When hydrogen gas is passed over, sulphuretted hydrogen gas is evolved, and pure metals remain behind. Of the metallic sulphurets which most frequently occur in nature, it is only the sulphurets of antimony, bismuth, and silver, that can be thus converted into reguline metals by a degree of heat insufficient to melt glass. A native compound of sulphuret of antimony with sulphuret of silver, known to mineralogists under the name of Ruby Silver (dunkles Rothgültigerz), can be converted in this manner into an alloy of silver and antimony. The two metals can then be separated and estimated, and what is wanted to make up the original weight can be estimated as sulphur. This method, however, can only be followed when the compound is free from the slightest traces of sulphuret of arsenic.

Separation of Sulphuret of Antimony from Oxide of Antimony.—When a substance to be examined consists of a metallic sulphuret, and an oxide of the same metal, the examination is easy, when both substances can, by being heated in an atmosphere of hydrogen gas, be converted into reguline metals. But, among all the metallic sulphurets which form compounds with oxides, this is the case with the sulphuret of antimony alone. The compounds of sulphuret of antimony with oxide of antimony can be decomposed by hydrogen gas, in an apparatus similar to that described at page 65. The sulphuretted hydrogen gas passes away, but the water produced by the combination of a portion of hydrogen with the oxygen of the oxide, is partly condensed in the glass bulb *g*, and partly absorbed by the chloride of calcium, which fills the tube *h*. The operator determines the quantity of the metal obtained, as well as that of the water which is formed, from which he easily finds the quantity of the oxide. The quantity of the sulphuret is calculated from that of the oxide. When the compound contains but a small quantity of oxide, or when but a small portion of the compound is taken for examination, the operator may dispense with the glass bulb *g*, and connect the glass tube of the bulb *e* immediaately with the tube *h*. This method of analysis is preferable to that in which the oxide of antimony is sought to be separated from the sulphuret of antimony, by means of a weak acid, or of an acid salt, such as cream of tartar. If the substance under examination be in a very finely-divided state, the sulphuret of antimony is capable of being decomposed by continued boiling with cream of tartar and water.

When the operator has to examine compounds of such metallic sulphurets with oxides as cannot, in this state, be reduced by hydrogen gas, he must treat them in the same manner as he is obliged to treat the simple metallic sulphurets. He digests a weighed portion of the compound with nitric acid or aqua regia, and determines the quantity of the sulphur and of the resulting sulphuric acid. He then has in solution the metallic oxide originally contained in the compound, and that produced by the action of the nitric acid. He determines the total quantity of oxide, and then calculates the relative proportions of sulphuret and of oxide contained in the compound submitted to analysis.

Quantitative Estimation of Sulphuric Acid.—In what manner the compounds of sulphuric acid, or the sulphates, are analysed, may partly be inferred from what has been already said upon that point. The soluble sulphates are dissolved in water, and the sulphuric acid is precipitated by a solution of a salt of barytes. The quantity of sulphuric acid is calculated from the weight of the precipitated sulphate of barytes. Before proceeding any farther with the analysis, it is proper to separate, by sulphuric acid, the excess of barytes remaining in the filtered solution. The operator then proceeds to estimate the quantity of the base which was combined with the sulphuric acid. When the sulphuric acid contained in a solution of a neutral sulphate is to be precipitated by a solution of chloride of barium, the solution of the sulphate must previously be acidulated by the addition of muriatic acid.

Analysis of insoluble Sulphates.—But when the sulphate to be examined is insoluble in water, which is the case, for example, with several basic sulphates, it must be dissolved in muriatic or nitric acid, the solution must be diluted with water, and then precipitated by a solution of barytes.

Separation of Sulphuric Acid from Barytes, Strontian, Lime, and Lead.—When, however, the sulphate is insoluble in acids, or at least is very slightly soluble therein, the analysis must be conducted in another way. Among the insoluble or difficultly soluble sulphates which are here alluded to, are the compounds of sulphuric acid with barytes, strontian, lime, and protoxide of lead. The sulphate of lime is completely decomposed when it is pulverised and boiled with an excess of a solution of carbonate of potash or carbonate of soda. The fixed product of this operation is carbonate of lime, which is insoluble and can be separated by filtration; it is washed, dried, and weighed. It can, after the weighing, be submitted to ignition; but, as it can lose a portion of its carbonic acid by being heated to redness, it is necessary to treat the ignited lime with a solution of carbonate of ammonia. Instructions respecting this operation have been given at page 17, in treating of the mode of estimating the oxalate of lime. The solution, filtered from the carbonate of lime, which, in addition to the alcaline sulphate, contains an excess of alcaline carbonate, is cautiously acidulated by muriatic acid, and then precipitated by a solution of chloride of barium. Hereupon, a precipitate of sulphate of barytes is obtained, from the weight of which the operator reckons the quantity of sulphuric acid.

The other sulphates, which are insoluble or difficultly soluble in water and in acids, can only be decomposed by carbonate of potash, or of soda, by being melted therewith. One part of the insoluble sulphate, reduced to very fine powder, is carefully mingled, in a platinum crucible, with three parts of carbonated alcali, and the crucible is exposed to such a heat as is sufficient to make the mixture melt. If sulphate of lead be present, care should be taken not to employ too strong or too long-continued a heat, otherwise a portion of lead might be separated in the reguline state, and this lead might combine with the platinum crucible and very much injure it. In this case, it is usual to employ such a degree of heat that the mass does not completely run together. The ignited mass is afterwards softened with water. If the compound contain no oxide of lead, but only barytes and strontian, the insoluble substances remaining, after treating the ignited mass with water, are carbonate of strontian and carbonate of barytes, which, after being washed, are dissolved in muriatic acid, and separated and estimated in the manner already particularized. The solution, filtered from the carbonated earths, contains the alcaline sulphate and the excess of the alcaline carbonate employed to effect the decomposition; this solution is supersaturated by muriatic acid, and the sulphuric acid is precipitated by a solution of chloride of barium. From the weight of the resulting sulphate of barytes, the operator calculates how much sulphuric acid was contained in the insoluble sulphate submitted to analysis.

If the sulphate submitted to analysis contained lead, then the solution, formed by treating the ignited mass with water, contains a trace of oxide of lead. When it is not intended to determine the quantity of sulphuric acid, this oxide of lead is precipitated, as sulphuret of lead, by directly applying bihydrosulphuret of ammonia. But if the operator desires to determine also the quantity of sulphuric acid in the solution, he supersaturates the liquid with nitric acid, and precipitates the sulphuric acid by a solution of nitrate of barytes. He then filters the solution from the sulphate of barytes and precipitates the trace of lead, as sulphuret of lead, by the addition of liquid sulphuretted hydrogen.—The substance which remains undissolved, when the ignited mass is treated with water, is protoxide of lead. When this protoxide is pure, it is ignited in a small porcelain crucible and afterwards weighed; but when it contains other substances, as, for example, peroxide of iron, it is dissolved in nitric acid, and the oxide of lead is then separated from the foreign substances which contaminate it, by the processes which have already been described.

Separation of Sulphuric Acid from Chromic Acid.—The separation of sulphuric acid from chromic acid, and of the sulphates from the chromates, is best effected as follows:—The compound is dissolved in a small portion of water, and after the addition of a sufficient quantity of muriatic acid, the solution is carefully boiled till it no longer produces the odour of chlorine. The solution is then diluted with water.

The operator can first precipitate the oxide of chromium by ammonia, and then, after filtering the solution and acidulating it by muriatic acid, precipitate the sulphuric acid, by a solution of a barytic salt, as sulphate of barytes, or, on the contrary, he can first precipitate the sulphuric acid by a solution of barytes, and afterwards, by ammonia, the oxide of chromium; yet, in the latter case, the excess of barytes must first be separated by the addition of sulphuric acid.—The addition of alcohol to the muriatic acid, for the purpose of hastening the reduction of the chromic acid to chromic oxide, dare not be made. Such an addition would render the determination of the quantity of sulphuric acid impossible.

Analysis of Hyposulphates and Hyposulphites in Solution.—The compounds formed by the other acids of sulphur with bases, can be best analysed by converting them, by oxidation, into sulphates, and then treating the sulphates according to the methods which have just been described. The oxidation of these compounds must, however, be effected with precaution. Supposing the operator to have a solution, it must be mixed with strong nitric acid or aqua regia, and digested, with the assistance of heat, for a considerable time. This is the only means of effecting a complete oxidation of the compound. When solutions of hyposulphates are acted upon in the cold, oxidation does not take place. To prevent any disengagement of sulphurous acid gas, it is proper to warm the solution of the substance to be oxidised, before the strong nitric acid is added: it is best to employ the fuming nitric acid for this purpose. The hyposulphites, when treated in this manner, deposit sulphur, which, however, upon continuing the digestion, is partly, and often completely, redissolved and converted into sulphuric acid.—It is necessary to treat in the same manner the solutions of the acids of sulphur which contain less oxygen than is contained in sulphuric acid.

Analysis of dry Sulphites, Hyposulphates, and Hyposulphites.—When the compounds formed by bases with the acids of sulphur which contain less oxygen than sulphuric acid, are presented for examination in the dry state, they are oxidised by strong nitric acid. If the operator has oxidised a sulphite, he can then, provided the base be not volatile, ignite it in a platinum capsule, and so convert it into a neutral sulphate. If, on the other hand, he has oxidised one of the hyposulphites or hyposulphates, he can only venture to ignite it, after having added a certain quantity of base to it; because the salts of hyposulphurous and hyposulphuric acids are converted, when treated with strong nitric acid, into sulphates with excess of acid.

Analysis of Hyposulphates.—To analyse dry hyposulphates, it is unnecessary to treat them first with nitric acid or aqua regia; all that is necessary is to expose a given quantity to ignition. The operator then obtains a neutral sulphate which can be weighed; sulphurous acid gas and water of crystallization escape during the ignition. The sulphuric acid contained in the neutral sulphate contains half the quantity of sulphur which was contained in the hyposulphuric acid of the compound analysed. Hence it is easy to calculate the quantity of hyposulphuric acid, and thence the quantity of the water of crystallization.

Separation of Sulphuric Acid from Hyposulphuric Acid, and from Sulphovinic Acid.—If several of the acids of sulphur are contained in one solution, and the respective quantities are to be estimated, the object can be effected by various processes.—If a solution contains sulphuric acid and hyposulphuric acid, and both in uncombined condition, the quantity of each can be best determined by the process which follows: The operator adds to the liquid a solution of pure barytes in excess and calculates the quantity of sulphuric acid from the weight of the sulphate of barytes; during the filtration of which, the solution and precipitate must be protected from the air. To get rid of the excess of barytes, the operator either passes a current of carbonic acid gas through the solution and then exposes it to heat, or else slowly evaporates the solution to dryness and treats the dry mass with water. In either case he separates the free barytes as an insoluble carbonate of barytes. He then filters the solution, and adds sulphuric acid as long as it occasions the precipitation of sulphate of barytes. He determines the quantity of barytes in the precipitated sulphate of barytes, and calculates how much hyposulphuric acid is necessary to saturate that quantity of base.—The analysis is conducted in the same manner when a solution, besides containing sulphuric acid, contains the compound of carburetted hydrogen with sulphuric acid, which is known by the name of sulphovinic acid, and which much resembles the hyposulphuric acid in its properties.

Separation of Sulphates from Hyposulphates.—When, however, the sulphuric acid and hyposulphuric acid are combined with bases, and the quantity of each acid is nevertheless to be determined, it is best to effect the analysis with two different portions of the compound. With one portion the operator determines the quantity of sulphuric acid in the ordinary manner; that is to say, by precipitating the solution by a solution of barytes, and calculating the quantity of sulphuric acid from the weight of the sulphate of barytes. He treats the other portion of the compound with nitric acid or aqua regia, for the purpose of converting the hyposulphuric acid into sulphuric acid, by the process of oxidation described above. When this is effected, he precipitates the solution by a salt of barytes, and determines the quantity of sulphuric acid. The difference in the two quantities of sulphuric acid, indicated by these two experiments, furnishes the data for determining the quantity of sulphuric acid produced by the oxidation of the hyposulphuric acid, and consequently the quantity of hyposulphuric acid contained in the compound submitted to analysis.

Separation of Sulphates from Sulphites.—When a compound contains both sulphates and sulphites, the respective quantities of the acids can be determined in a similar manner. But in this case, to facilitate the determination of the sulphuric acid, it is necessary before the precipitation is effected, to acidulate the solution with muriatic acid.

XLI. PHOSPHORUS.

Quantitative Estimation of Phosphoric Acid.—Phosphoric acid can be quantitatively estimated in the same manner as arsenic acid; but the solution in which it is dissolved must contain nothing else, except nitric acid, which can do no harm. The operator adds to the solution an accurately weighed quantity of pure and recently ignited protoxide of lead; he then evaporates the whole to dryness and ignites the residue in a small counterpoised platinum capsule. The quantity of dry phosphoric acid is found by deducting the original weight of the protoxide of lead from the weight of the ignited mass.—The estimation of phosphoric acid likewise requires that the solution contain no other acid which can form a salt of lead incapable of reduction, by ignition, to pure protoxide of lead.

Quantitative Estimation of Phosphorous Acid and Hypophosphorous Acid.—Phosphorous acid and hypophosphorous acid, contained in solutions, can be quantitatively estimated in a similar manner. The operator adds to the solution a weighed quantity of protoxide of lead, and, at the same time, as much nitric acid as is necessary to raise the phosphorous and hypophosphorous acids to the highest degree of oxidation. When the whole has been reduced by evaporation to a very small volume, it is washed into a small weighed platinum capsule and evaporated to dryness; the dry mass is then ignited, and the remainder is weighed. This residual matter consists of phosphoric acid and protoxide of lead. The weight of the latter being known, can be deducted, which gives the weight of the phosphoric acid. It is then necessary to calculate how much phosphorous or hypophosphorous acid is equivalent to this weight of phosphoric acid.—The phosphorous or hypophosphorous acid becomes fully converted into phosphoric acid during the ignition; the oxidation is produced by the nitrate of lead, which decomposes at that period. The ignition must be performed with caution; because the mass swells up when heated, and a loss can easily be occasioned by incautious management. A loss can be also occasioned, during the ignition, when too great a quantity of protoxide of lead has been employed; for in that case too great a quantity of nitrate of lead is formed, and this salt has the disagreeable property of strongly decrepitating before undergoing decomposition.

Separation of Phosphoric Acid from Bases.—The separation of phosphoric acid from other substances is frequently accompanied by the greatest difficulties. The most accurate method of determining, in the analysis of the phosphates, the quantity of phosphoric acid they contain, consists in determining the quantity of the base, or substance combined with the phosphoric acid, contained in a weighed quantity of a given phosphate; the quantity of the phosphoric acid is then found from the loss.

Separation of Phosphoric Acid from Sulphuric Acid.—Phosphoric acid can be very accurately separated from sulphuric acid, by the solution of a salt of barytes, added in excess to an acid solution. Sulphate of barytes then precipitates, while phosphate of barytes remains in solution. The weight of the sulphate of barytes indicates the quantity of sulphuric acid. The quantity of phosphoric acid contained in the filtered solution, can now be found by saturating the solution with ammonia, whereby the phosphate of barytes is precipitated: this is not a method, however, which affords an accurate result. Supersaturation with ammonia does not effect the complete precipitation of the phosphate of barytes; on the contrary, a portion of barytes remains in solution, and the more acid the solution was, the greater is the portion of barytes which remains dissolved; for, upon saturating the acid with ammonia, a large quantity of an ammoniacal salt is produced, and this it is that dissolves the phosphate of barytes. It is when muriatic acid is contained in the solution that the quantity of phosphate of barytes which escapes precipitation is by no means inconsiderable. Phosphate of barytes is, indeed, so extremely soluble in a solution of muriate of ammonia, that, when a solution of chloride of barium is added to a solution of phosphoric acid, which contains a very large quantity of muriatic acid, and the mixture is supersaturated with ammonia, it very often happens, that not the smallest precipitate of phosphate of barytes is produced.

Separation of Phosphoric Acid from the Oxides of Arsenic, Tellurium, and Selenium.—The separation of phosphoric acid from the acids of arsenic is very well effected by sulphuretted hydrogen gas, which, on being led through an acid solution, precipitates the acids of arsenic, in the state of sulphuret of arsenic, but has no action on the phosphoric acid. The operator then determines, from the weight of the resulting sulphuret of arsenic, the quantity of the arsenious or arsenic acid. The particulars of this operation have been given above, at page 199. If the operator intends to determine the quantity of phosphoric acid existing in the solution filtered from the sulphuret of arsenic, he must effect that object by means of protoxide of lead, in the manner described above. It stands for itself, that the solution must contain no other acid capable of forming a fixed salt with protoxide of lead; it may contain nitric acid, because the nitrate of lead is decomposed by heat; but it must not contain the least trace of sulphuretted hydrogen gas, the excess of which must therefore be carefully separated before the addition of the protoxide of lead. —By the same process, the phosphoric acid could be separated from the oxide of tellurium and from selenious acid, should these substances occur in combination with it; yet it would be still better to separate them by treatment with sulphurous acid.

Separation of Phosphoric Acid from the Oxides of Cadmium, Lead, Bismuth, Copper, Silver, Mercury, Tin, and Antimony, by Sulphuretted Hydrogen Gas.—When phosphoric acid is combined with the oxides of cadmium, lead, bismuth, copper, silver, mercury, tin, or antimony, a weighed quantity of the compound is dissolved in an acid, for which purpose the acid which it is best to take, in most cases, but not when the oxides of lead and silver are present, is muriatic acid. The solution is diluted with water, and the metallic oxide is then precipitated by a current of sulphuretted hydrogen gas. The resulting metallic sulphuret is treated according to the methods which have been already described, with a view to determine the equivalent proportion of oxide. The quantity of the phosphoric acid is estimated from the loss.

Separation of Phosphoric Acid from the Oxides of Silver and Lead.—When phosphoric acid is combined with the oxides of silver and lead, another mode of operating may be adopted. The compound can be dissolved in nitric acid, and the oxide of silver precipitated by muriatic acid. From the weight of the resulting chloride of silver, the quantity of the oxide of silver is calculated. The quantity of the phosphoric acid is then easy of inference. —If protoxide of lead be contained in the nitric acid solution of the phosphate, it is precipitated by sulphuric acid. The addition of alcohol to the solution occasions the entire precipitation of the sulphate of lead, since that salt is quite insoluble in a spirituous solution. From the weight of the resulting sulphate of lead, the quantity of the protoxide of lead is calculated. The quantity of the phosphoric acid is then inferred from the loss.

Analysis of Compounds containing Phosphoric and Arsenic Acids, in combination with the Oxides of Cadmium, Lead, Bismuth, Copper, Silver, Mercury, Tin, and Antimony.— If the compound for analysis consists of phosphoric acid and arsenic acid, combined with one of the metallic oxides which are precipitable from acid solutions by sulphuretted hydrogen gas, the analysis may be performed by two different methods. Compounds of the kind alluded to occur in nature; and as the phosphoric acid and arsenic acid are isomorphous, they replace each other in these compounds in ever-varying proportions.—The compound is dissolved by an acid. In most cases muriatic acid, but in a few cases nitric acid, forms the most appropriate solvent. According to one of the methods of analysis, the solution is diluted with a sufficient quantity of water, and the metallic oxide and the arsenic acid are precipitated together by sulphuretted hydrogen gas, as metallic sulphurets. The sulphuret of arsenic is then separated from the other metallic sulphuret, and the equivalent proportions of arsenic acid and metallic oxide are estimated or reckoned. According to the other method of analysis, the acid solution is supersaturated with ammonia, and then mixed with such a quantity of bihydrosulphuret of ammonia as is merely sufficient to precipitate the metallic oxide. After filtration from the metallic sulphuret, the sulphuret of arsenic can be precipitated by muriatic acid. This method dare not be adopted when the oxides of tin and antimony are contained in the compound, since the sulphurets of these metals, like the sulphuret of arsenic, are soluble in an excess of bihydrosulphuret of ammonia. As the measures of precaution which are necessary to be taken, in examinations of this nature, have been minutely detailed in their proper places, it is useless to repeat the description here. When the quantity of the arsenic acid and of the metallic oxide has been determined by the above experiments, the quantity of the phosphoric acid, which is affected neither by the sulphuretted hydrogen gas, nor the bihydrosulphuret of ammonia, is calculated from the loss.—If the compound for analysis contain phosphoric acid, arsenious acid, and one of the above-named metallic oxides, the operation proceeds exactly in the same manner.

Separation of Phosphoric Acid from the Oxides of Cobalt, Zinc, Iron, Manganese, Cadmium, Lead, Bismuth, Copper, Silver, and Mercury, by Bihydrosulphuret of Ammonia.— When phosphoric acid is combined with the oxides of cobalt, zinc, iron, or manganese, the compound is best analysed as follows: A weighed quantity of the phosphate is dissolved in an acid, and the acid which answers best is muriatic acid; the solution is supersaturated with ammonia, and the metallic oxides are precipitated by bihydrosulphuret of ammonia, as metallic sulphurets. Upon saturating the muriatic acid solution of these phosphates with ammonia, the phosphate itself is at first precipitated; but, in some cases, it redissolves in the excess of ammonia. It is, however, a matter of no importance whether it redissolve or not; for, even when precipitated, the phosphate is completely decomposed by digestion with bihydrosulphuret of ammonia; so that the resulting metallic sulphuret is totally free from phosphoric acid. From the weight of the metallic sulphuret it is easy to calculate the quantity of the metallic oxide which existed in the compound. The quantity of the phosphoric acid is then indicated by the loss.—It is possible to analyse, in the same manner, the compounds of phosphoric acid with the oxides of cadmium, lead, bismuth, copper, silver, and mercury. It would be ridiculous, however, to analyse the compounds of phosphoric acid with the oxides of lead and silver by this process, since the method formerly described of quantitatively estimating these compounds is so much simpler.

Separation of Phosphoric Acid from the Oxides of Chromium, Uranium, Nickel, &c., by Fusion with Carbonate of Potash.—The compounds formed by the combination of phosphoric acid with metallic oxides which are incapable of precipitation, either from acid solutions by sulphuretted hydrogen gas, or from ammoniacal solutions by bihydrosulphuret of ammonia,—such, for example, as the oxides of chromium, uranium, and nickel,—are more difficult of examination. When the compound to be analysed is that formed by oxide of nickel with the phosphoric acid, the operator might dissolve it in muriatic acid, saturate the solution with ammonia, and act on it with bihydrosulphuret of ammonia. By this means the oxide of nickel would be thrown down as sulphuret of nickel; yet this process, as was observed at page 91, is not without its difficulties. When the compounds to be analysed are those formed by phosphoric acid with the oxides of chromium and uranium, this method is altogether out of the question. To estimate, therefore, the quantity of the metallic oxides contained in compounds of this description, it is necessary to operate as follows: A weighed quantity of the compound is mixed, in a large platinum crucible, with about three times its weight of dry carbonate of potash or carbonate of soda, and the mixture is submitted to ignition. The ignited mass is afterwards treated with water, in which the resulting alcaline phosphate and the excess of alcaline carbonate dissolve, while the metallic oxides remain undissolved. The precipitate is washed with water and weighed. The quantity of the phosphoric acid, which was previously combined with the metallic oxides, is indicated by the loss.—The precipitated metallic oxides must always be redissolved in muriatic acid and be again precipitated; for they commonly contain alcali in quantity by no means inconsiderable, and which it is impossible to separate from them by washing. This is particularly the case, when this process is employed to separate peroxide of uranium from phosphoric acid, since peroxide of uranium forms a chemical compound with the potash or soda employed. This compound must be dissolved in muriatic acid, from which peroxide of uranium can be precipitated by ammonia. The precipitate is washed with a solution of muriate of ammonia, heated to redness, and then weighed.—BERZELIUS employed this method of separating phosphoric acid from peroxide of uranium, when engaged in the analysis of the mineral called Uranite.

The separation of phosphoric acid from metallic oxides can be effected in a great number of cases by the above method of fusion with an excess of carbonate of potash or carbonate of soda. It is essential to the success of the operation that the metallic oxides contained in the phosphates thus analysed, be perfectly insoluble in carbonated and caustic potash. It is better, however, in most cases, to precipitate the metallic oxides by sulphuretted hydrogen gas or bihydrosulphuret of ammonia, which methods not only effect a more accurate separation, but one which is accompanied by fewer difficulties.

Separation of Phosphorus from Copper, Iron, Nickel, and Cobalt.—The compounds of phosphorus with such metals as are precipitable from their solutions by sulphuretted hydrogen gas or by bihydrosulphuret of ammonia, are treated with nitric acid or aqua regia, with the help of heat. They are then completely dissolved, even when they contain much phosphorus, of which they leave no residue. The solution is afterwards treated in the same manner as an acid solution of a metallic phosphate. There are, however, but few metals which combine with phosphorus to form phosphurets. These are chiefly copper, iron, nickel, and cobalt; yet these four metals combine with phosphorus in a great variety of proportions.—The phosphurets of the metals which, with the assistance of an acid, are able to decompose water, such as iron, nickel, and cobalt, are not in the least acted on by muriatic acid, not even when heated.

Separation of Phosphoric Acid from the Earths.—The separation of phosphoric acid from the non-alcaline earths is often accompanied by extraordinary difficulties. The phosphates of these earths are so similar to the pure earths, that even the most distinguished chemists have, and that in quantitative analyses too, quite overlooked a considerable proportion of phosphoric acid.

Separation of Phosphoric Acid from Yttria.—Phosphoric acid forms with yttria, a compound which occurs in nature. To separate these two substances, BERZELIUS (POGGENDORFF'S Annalen, B. III. p. 204) directs us to melt the compound with carbonate of soda. The melted mass is afterwards treated with water, which dissolves the phosphate and carbonate of soda, and leaves the yttria undissolved.

Separation of Phosphoric Acid from Alumina.—Most particularly difficult is the separation of phosphoric acid from alumina. The phosphate of alumina behaves towards caustic potash, pretty nearly like pure alumina, so that no separation can thus be effected. Neither can phosphoric acid be separated from alumina by fusion with carbonate of soda, because phosphate of alumina is soluble in a solution of carbonate of soda. According to BERZELIUS (*Annales de Chimie et de Physique*, T. XII. p. 15), the analysis of this compound can be successfully performed as follows: The proper quantity of the compound is first finely pulverised and weighed. It is then mingled in a platinum crucible with very finely pulverised and pure silicic acid, and with carbonate of soda. The mixture is afterwards exposed for half an hour to a red heat. If the compound consists chiefly of phosphoric acid and alumina, the mixture must be made in such a manner that two parts of the compound be accompanied by one and a half parts of silicic acid, and about six parts of carbonate of soda. The silicic acid obtained in the analysis of silicates is best adapted to this use; but if that should be wanting, finely-levigated rock crystal may be employed in its place, and answers nearly as well. The ignited mass is digested with water, the insoluble matter is filtered, and washed with water. The solution contains phosphate of soda, and the excess of carbonate of soda. The residue consists of silicic acid combined with alumina and soda. A small quantity of silicate of soda is, however, contained in the solution. To precipitate this portion, the solution is digested with a little carbonate of ammonia. The small precipitate then produced is added to the mass which was filtered from the aqueous solution. The mass is then treated with muriatic acid, and the whole is evaporated to perfect dryness. The silicic acid is thereby rendered insoluble. A capsule of platinum or porcelain is employed for this evaporation. The dry mass is moistened, in a uniform manner, with muriatic acid, and after some time, is treated with water. The whole of the silicic acid employed then remains undissolved. The alumina dissolves, and is precipitated from the filtered solution by carbonate of ammonia. If any other bases are present, they will be dissolved with the alumina. The quantity of the phosphoric acid is commonly estimated from the loss, provided the compound contain no other acid capable of forming a soluble salt with soda. If, however, the operator wishes to determine the quantity of the phosphoric acid by a direct experiment, and with all the accuracy that the case admits of, he must employ the methods which will be described farther on.

The method employed by FUCHS, to separate phosphoric acid from alumina (SCHWEIGGER's Jahrb. T. XXIV. p. 127), is the following: The weighed compound is dissolved in a solution of caustic potash, and to this solution, a solution of silicate of potash (liquor of flints) is added. This produces a thick slimy mass, which is diluted with water, and made to boil. A strong precipitate is then produced, which is a silicate of alumina and potash. This precipitate is treated with muriatic acid, and the siliceous jelly produced is evaporated to dryness. The silicic acid is then separated in the same manner as in the process of BERZELIUS. The liquid having been filtered from the silicic acid, the alumina is precipitated by carbonate of ammonia.—The solution filtered from the silicate of alumina and potash contains the whole of the phosphoric acid which existed in the phosphate of alumina.

Separation of Phosphoric Acid from Magnesia.—Phosphoric acid could probably be separated from magnesia by igniting the compound with carbonate of potash, and treating the ignited mass with water. But it has not yet been determined by experiment, whether this method of separation is followed by accurate results.

Separation of Phosphoric Acid from Lime, Barytes, and Strontian.—The separation of phosphoric acid from lime, barytes, and strontian, is accompanied by no difficulties. It is, on the contrary, easy to obtain very accurate results. A weighed quantity of the compound is dissolved in an acid, and that most adapted to this object is muriatic acid. If, now, the phosphoric acid is combined with barytes only, the acid solution is diluted with water, and the barytes is precipitated by sulphuric acid. From the weight of the precipitated sulphate of barytes, it is easy to reckon the quantity of barytes. The quantity of the phosphoric acid is, in this process, to be inferred from the loss.—When, on the contrary, the phosphoric acid is combined with strontian or lime, then alcohol, instead of water, is added to the muriatic acid solution. The earths are afterwards precipitated by sulphuric acid. The resulting sulphates are quite insoluble in alcohol, and are therefore completely precipitated from the solution. The precipitate is filtered, edulcorated with alcohol, and then ignited. After ignition, the weight is determined, and the quantity of strontian or lime is calculated. The quantity of the phosphoric acid is estimated from the loss.

Separation of Phosphoric Acid from Potash and Soda.—Even when the phosphoric acid is combined with the two alcalies, potash and soda, its quantitative estimation is, according to MITSCHERLICH (*Annales de Chimie et de Physique*, T. XIX. p. 369), still best effected by determining the quantity of the base by experiment, and inferring the quantity of the phosphoric acid from the loss. The method of operating is as follows: A weighed quantity of the phosphate is dissolved in water, and a solution of acetate of lead is added in excess. The phosphoric acid combines with the protoxide of lead, and is fully precipitated, even when the compound under analysis is an acid phosphate; because the phosphate of lead is almost utterly insoluble in acetic acid. The resulting precipitate is filtered. The excess of protoxide of lead could be separated from the filtered solution by a current of sulphuretted hydrogen gas, which would throw down sulphuret of lead; but it is better, because less circumstantial, to mix the solution with a solution of carbonate of ammonia, and to expose the whole to heat. The excess of lead is thereby precipitated as carbonate of lead. The solution is separated by filtration, and evaporated to dryness; what then remains is heated to redness. The result is a carbonated alcali, which must be weighed. But when the weighing cannot be effected with great accuracy, as is the case when the substance is carbonate of potash, the substance is treated with muriatic or sulphuric acid, and the resulting chloride or sulphate is evaporated, ignited, and weighed. The quantity of the alcali is then reckoned, while the quantity of the phosphoric acid is inferred from the loss.—The precipitation of the phosphoric acid cannot be so well effected by a solution of chloride of barium, as by the acetate of lead; for the phosphate of barytes is not quite insoluble in water, and when the substance analysed is an acid phosphate, the solubility of the resulting phosphate is considerably increased, so that it becomes necessary to add ammonia to the solution. The excess of barytes can, moreover, not be so effectually removed by carbonate of ammonia, as by sulphuric acid. If it be precipitated by sulphuric acid, and if ammonia has previously been added to the solution, to facilitate the precipitation of the phosphate of barytes, then a quantity of sulphate of ammonia is produced. The evil which hence results is, that it is very difficult to separate the sulphate of ammonia from the fixed alcaline sulphate, without suffering a loss by the ignition.

Separation from Lithia.—Great difficulties attend the separation of phosphoric acid from lithia, particularly when soda is also present. BERZELIUS (POGGENDORFF'S Annalen, B. IV. p. 247), has employed the following method of decomposing these compounds: A weighed quantity of the compound is mingled and melted in a platinum crucible, with twice its weight of carbonate of lime. The melted mass is carefully pulverized, and then boiled with water. The liquid then contains lime, with the whole quantity of the alcalies, in the state of carbonates, while phosphate of lime remains undissolved. The solution is now saturated with oxalic acid, the oxalate of lime is filtered, the solution is evaporated to dryness, and the dry mass is ignited. The carbonated alcali thus obtained is next weighed. If the compound contain soda or potash, it must be separated from the lithia by the process described at page 11.

Analysis of Phosphates containing several Bases.—The analysis of the phosphates becomes difficult, when the phosphoric acid is combined with several bases at once; unless, indeed, these bases can be all precipitated as metallic sulphurets, either from acid solutions by sulphuretted hydrogen gas, or from neutral solutions by bihydrosulphuret of ammonia. A case of this sort is presented, when the phosphoric acid is combined at once with a metallic oxide and with an earth. The analysis is then effected as follows: A weighed quantity of the compound is ignited with carbonate of potash or carbonate of soda, and the ignited mass is treated with water. This, in most cases, dissolves only the excess of carbonate of alcali, and the newly-formed phosphate of alcali. The bases, with which the phosphoric acid was previously combined, remain behind undissolved: they are dissolved in muriatic acid, and separated according to methods which have been already described.—According, however, to this method of analysing the phosphates, it is impossible to separate alumina from such metallic oxides as can only be precipitated from neutral solutions by bihydrosulphuret of ammonia.—To separate the bases which occur together in compounds that contain phosphate of lime with protophosphate or perphosphate of iron, BERZELIUS (Jahresbericht, 1822, p. 121) employs a method which was first recommended by HERSCHEL (Edinburgh Phil. Journ. V. VI. p. 300), for the separation of peroxide of iron from other oxides. The compound is dissolved in an acid, and the iron, if in the state of protoxide, is oxidised by nitric acid to peroxide. Thereupon, the liquid is saturated as accurately as possible with a solution of carbonate of ammonia; or rather, so much of the solution is added, that a slight precipitation begins to be produced. The mixture is then boiled. The peroxide of iron is thereby precipitated, while the phosphate of lime remains in solution. This method is grounded upon the fact, that the neutral salts of peroxide of iron are precipitated from their solutions by boiling. But as a small portion of peroxide of iron can remain in solution, in consequence of the presence of a little free acid, it is proper to add a small quantity of alcali to the filtered solution, and to boil it again, until it has become so slightly acid, that peroxide of iron can no longer remain dissolved in it. As the precipitated basic salt of peroxide of iron has often the propensity to pass through the filter, BERZELIUS has found it to be advantageous, to clear the solution with a few drops of a solution of isinglass, which makes the peroxide of iron conglobe better. The precipitated peroxide of iron always contains phosphoric acid. It must, therefore, be redissolved in muriatic acid. The solution is saturated with ammonia, and the iron is precipitated, as sulphuret of iron, by bihydrosulphuret of ammonia. The solution in which the lime is dissolved, is concentrated by evaporation; after which, the lime is precipitated by sulphuric acid and alcohol.

Method of Analysing the Phosphates which are insoluble in Acids.—In the analysis of the phosphates, it must always be borne in mind, that although all acid, neutral, and basic compounds of phosphoric acid are soluble in acids, yet a great number of acid phosphates become insoluble in muriatic acid, nitric acid, and diluted sulphuric acid, when they have been heated to redness. An insoluble phosphate of this description can be decomposed by melting a weighed portion of it, with three times its weight of carbonate of potash or carbonate of soda, and subsequently treating the melted mass with water. But the following mode of operating is less circumstantial: The insoluble compound is pulverised, and a weighed quantity of it is placed in a pretty large platinum capsule. Concentrated sulphuric acid is poured over it, and the whole is boiled for a considerable time, yet care must be taken not to allow the excess of sulphuric acid to evaporate entirely. Water is afterwards added with caution, upon which the compound completely dissolves, provided the base of the phosphate is not one of those whose compounds with sulphuric acid are either insoluble or but difficultly soluble; such, for example, as protoxide of lead, lime, strontian, or barytes.

Precipitation of Phosphoric Acid by Solutions of Lead, Lime, and Barytes.—In none of the methods of separating the phosphoric acid from bases which have hitherto been treated of, has it been mentioned in what manner the quantity of the phosphoric acid can, in the examination of the phosphates, be directly determined by experiment. The direct determination of phosphoric acid cannot be effected with such accuracy as that of many other substances; and the analysis of the phosphates which unquestionably give the most accurate results, are those in which the quantity of the base is determined by experiment, and the quantity of the phosphoric acid is estimated from the loss. In many cases, however, particularly when a great number of bases are present, it can be of use, to determine the quantity of the phosphoric acid by experiment. If the base has been separated from the phosphoric acid by sulphuretted hydrogen gas, and every trace of the sulphuretted hydrogen has been expelled, by a long-continued heat, from the acid solution filtered from the precipitated metallic sulphuret, then the quantity of the phosphoric acid can be estimated as follows: The solution is saturated with ammonia, and is then mixed with the solution of a salt, with the base of which the phosphoric acid can form an insoluble compound. The substances commonly chosen for this purpose are acetate or nitrate of lead, chloride of barium, or chloride of calcium. The solutions of the lead salts are, upon the whole, the best precipitants of phosphoric acid; when they are employed, it is proper to saturate the solution accurately with ammonia. When the acid solution has been supersaturated with ammonia, it can, indeed, be still precipitated by a solution of chloride of barium or chloride of calcium; but, in that case, the phosphate of lime or phosphate of barytes must be rapidly filtered, and must, during the filtering, be carefully sheltered from the air, otherwise it can easily be contaminated by carbonate of the same earth. It has been already mentioned, that the phosphate of barytes is not altogether insoluble in a liquid which contains ammoniacal salts. The phosphate of lime appears to be less soluble than that of barytes in such a solution; and on this account, a solution of chloride of calcium is better adapted than one of chloride of barium, to the precipitation of phosphoric acid. If the base has been separated from the phosphoric acid by bihydrosulphuret of ammonia, the solution filtered from the metallic sulphuret is acidulated by muriatic acid, and is warmed until every trace of sulphuretted hydrogen is expelled. The precipitated sulphur is then filtered, and the phosphoric acid is precipitated in the manner described above.—If the solution from which the phosphoric acid is to be precipitated contains carbonate of alcali, or even caustic alcali, it must be acidulated by muriatic acid, and the vessel which contains it, after being loosely covered, must be set aside for some time (about twenty-four hours), to afford the free carbonic acid an opportunity to escape. The precipitation of phosphoric acid from an ammoniacal solution by chloride of calcium, is best performed in a glass which can be closed by a cork. It is thereby protected from the action of atmospheric air, and the production of carbonate of lime is effectually prevented. The phosphate of lime is allowed to subside properly in the flask, the supernatant liquid is then filtered, and finally the precipitate is brought upon the filter, and edulcorated.

One can never tell, with certainty, what is the composition of the precipitates which have been thrown down from solutions of phosphates, by salts of lead, lime, or barytes. It is therefore impossible to reckon the quantity of the phosphoric acid, from the weight of the resulting precipitate. This is particularly the case, when phosphate of barytes, or phosphate of lime, has been precipitated from an ammoniacal solution, by chloride of barium or chloride of calcium; for the precipitate then consists of a mixture of neutral and basic salts in indeterminate proportions. The consequence of this is, that the quantity of the phosphoric acid contained in the precipitates, has, in all cases, to be determined by experiment. This examination is effected in the simple manner which has been mentioned above. The precipitate, after ignition, is first treated with sulphuric acid, and then, if it consist of phosphoric acid and barytes, with water. But when protoxide of lead, or lime, has been used to precipitate the phosphoric acid, the mixture of the precipitate with sulphuric acid, must be diluted with spirits of wine instead of water. The weight of the resulting sulphate is then determined, and the quantity of the barytes, lime, or protoxide of lead is calculated. Knowing the weight of the base, the operator finds with ease the weight of the phosphoric acid which was combined with it.

Quantitative Separation of Phosphates from Sulphates.—The quantitative estimation of phosphoric acid becomes still more uncertain, when the compound contains sulphuric acid. The sulphuric acid can, it is true, be easily separated by the solution of a salt of barytes, which reagent, as has been remarked above, precipitates sulphuric acid from an acid solution, but can precipitate phosphoric acid only from a neutralised solution. But when the sulphuric acid has been precipitated by barytes, it is not possible, for the reasons already mentioned, to throw down the whole of the phosphate of barytes, by supersaturating the filtered solution with ammonia. The joint quantitative estimation of sulphuric acid and phosphoric acid scarcely ever succeeds, except when the acids are combined with metallic oxides which can be precipitated from acid solutions by sulphuretted hydrogen gas. In this case, the compound is dissolved in nitric acid, the solution is diluted with water, and the metallic oxides are precipitated as metallic sulphurets, by sulphuretted hydrogen gas. The solution is filtered, the free sulphuretted hydrogen is expelled, and the sulphuric acid is precipitated by a solution of nitrate of barytes. The precipitated sulphate of barytes is weighed, and the quantity of the sulphuric acid is calculated. The solution filtered from the sulphate of barytes, is now cautiously evaporated to dryness, and the dry residue is ignited and weighed. Thereupon, it is necessary to determine how much barytes the dry residue contains, in order to be able to find the quantity of the phosphoric acid from the loss: to this end, the ignited mass is decomposed by sulphuric acid, and the quantity of the barytes is calculated from the weight of the resulting sulphate of barytes. Great care must be taken, in adding the nitrate of barytes, to add very little more than what is necessary to precipitate the sulphuric acid. The quantity of the excess which it is proper to add, is regulated by the quantity of the phosphoric acid. When too much nitrate of barytes has been employed, great disadvantages are produced. During the ignition, for example, when the excess of nitrate of barytes is decomposed, the access of atmospheric air gives rise to the production of carbonate of barytes. This is, of course, obtained, after the ignition, in a state of mixture with the phosphate of barytes, and being weighed with that substance, gives an incorrect result.

Separation of Phosphoric Acid from Bases by Caustic Potash.—A practice often followed in the examination of phosphates, is that of precipitating the bases by an excess of caustic potash, and separating them thus from the phosphoric acid. But the results afforded by this method are just as far short of accuracy as the results afforded by treating the arseniates with caustic potash (page 204). It very seldom happens, that, by the employment of ever so great an excess of caustic potash, the phosphoric acid can be fully separated from the precipitated metallic oxides.—The method, too, according to which the phosphoric acid is precipitated by the solution of a salt of lead, previous to the precipitation of the base of the phosphate, is, as has already been shown in the preceding pages, as little worthy of employment here, as a similar process in the analysis of the arseniates (page 204).

Method of Analysing the Phosphites and Hypophosphites.—When the compounds formed by the phosphorous and hypophosphorous acids with bases are to be analysed, they must, in the first place, be converted into phosphates, and then examined by the processes which have been given above. The best way to convert the phosphites and hypophosphites into phosphates is, to put a weighed quantity of the compound into a small shallow platinum capsule, to pour nitric acid over it, to evaporate the whole to dryness, and cautiously to ignite the remainder. When treated in this manner, the neutral phosphites yield neutral phosphates, while the neutral hypophosphites yield acid phosphates.—The quantitative estimation of the phosphites would be very simple, were it only necessary to dissolve the compound in water or in an acid, and then to determine the quantity of the base alone. But since all the phosphites contain water, which cannot be expelled by a gentle heat, and is essential to the existence of those salts, it follows that what is learned by precipitating the base of the phosphites, is not the quantity of the phosphorous acid merely, but that of the acid and the water taken together. It is necessary, therefore, to convert a weighed quantity of the phosphite into phosphate, to ascertain the weight of the phosphate, and then to determine the quantity of the base. By this process, the operator finds how much phosphoric acid has been produced by oxidation, from which he can easily reckon the quantity of the phosphorous acid which has been oxidised; and when he has thus found the quantity of the base and the acid contained in the phosphite submitted to analysis, he infers what must be the quantity of the water, from the loss of weight. —The compounds of the phosphorous acid with alcalies are soluble in water. The compounds of the same acid with other bases are only soluble in acids.

The hypophosphites are all soluble in water; the bases can therefore be precipitated from the solutions, and quantitatively estimated by the usual processes. When the hypophosphorous acid is combined with metallic oxides, the metallic oxides can even be precipitated by alcalies, provided they be such as alcalies are capable of precipitating. When earths are combined with the hypophosphorous acid, they may be thrown down by their appropriate precipitants, in the manner described in the foregoing sections.—If the operator, in analysing such salts, wishes to determine the quantity, not only of the acid but of the water, of which sometimes the whole, sometimes but a portion, is necessary to the existence of the salt, the method after which he must operate is as follows: A weighed quantity of the compound is mixed with nitric acid, and evaporated with it to dryness; the dry mass is then ignited.

The hypophosphorous acid is thereby oxidised. The compound is now weighed; after which, the quantity of its base is determined experimentally, and the quantity of the phosphoric acid produced by the oxidation of the hyhophosphite is reckoned from the loss. When the quantity of the phosphoric acid has been thus ascertained, that of the hypophosphorous acid which served to produce it, is learned by calculation. The quantity of the water contained in the substance examined is indicated by the loss. But in operating in this manner, we stumble upon a singular difficulty. The hypophosphites, when treated with nitric acid, are converted into acid phosphates. The latter, after ignition, become insoluble in muriatic acid, and are consequently difficult of decomposition. To render them soluble, it is necessary to treat them with sulphuric acid, in the manner which has been described above. Or, to prevent the difficulty, the hypophosphite to be analysed, may, before being exposed to the action of nitric acid, be mixed with a weighed quantity of base.

Separation of Phosphoric Acid from Phosphorous Acid or Hypophosphorous Acid.—When phosphoric acid and phosphorous acid, or phosphoric acid and hypophosphorous acid, are contained together in a solution, and the quantity of each is to be determined, the operation can be accurately effected as follows: The solution is poured by degrees and in small quantities, into a solution of perchloride of mercury, which must be fully saturated. This caution is necessary, because if a large quantity of the acid solution under examination were to be poured at once into the solution of perchloride of mercury, or if, on the contrary, the latter solution were to be poured into the former, then the mercury could be easily separated in the metallic state, an occurrence which must be particularly guarded against. When the operation is properly performed, there soon begins to fall down a precipitate of protochloride of mercury, exhibiting the splendour of mother of pearl; this precipitate gradually increases in quantity; yet, it is necessary to expose the solution to a warm digestion for a great number of days together, as the protochloride of mercury does not otherwise completely precipitate. The protochloride of mercury is then gathered upon a weighed filter, and dried by exposure to a moderate heat until it ceases to lose weight; its weight is then finally determined. From the weight of the resulting protochloride of mercury, it is easy to calculate how much oxygen has been taken up by the phosphorous or hypophosphorous acid, to effect its conversion into phosphoric acid; hence the quantity of the phosphorous or hypophosphorous acid can be readily inferred. The said quantity of oxygen is equivalent to the quantity of chlorine contained in the protochloride of mercury; for the perchloride of mercury, on being converted into protochloride of mercury, loses precisely the half of its chlorine.—Another quantity of the liquid for analysis is treated with nitric acid and a weighed quantity of protoxide of lead, precisely in the manner which has been described at page 249. The object of this operation is, to determine the quantity of the phosphoric acid which is either already formed in the solution, or can be produced by the phosphorous or hypophosphorous acid it contains, at the expense of the nitric acid which furnishes the requisite oxygen. As the operator learns, from the first operation, how much phosphoric acid is produced by the phosphorous or hypophosphorous acid of the solution, he has only to deduct this from the whole quantity of phosphoric acid indicated by the second operation, to learn the actual proportion of phosphoric acid contained in the liquid submitted to analysis.—This method is adapted to the analysis of the acid produced by the deliquescence of phosphorus in moist air. It never happens, that the three acids of phosphorus are contained in the same solution, and have to be individually estimated.

Separation of Phosphates from Phosphites or Hypophosphites.—When compounds of phosphates with phosphites or hypophosphites are to be examined, they must be dissolved in water, or if not soluble in water, in muriatic acid. The solution, in the first case, must be acidulated by muriatic acid. The operation is then proceeded with, in the manner just described.

XLII. SILICIUM.

Separation of Silicic Acid by Evaporation.—The quantity of silicic acid contained in an alcaline or acid solution can be determined by only one method: This consists in evaporating the solution to perfect dryness, to render the silicic acid insoluble. When the solution is alcaline, it must, previous to the evaporation, be acidulated by muriatic acid. The dry mass is afterwards treated with water, upon which the silicic acid remains undissolved. It is filtered, edulcorated, and ignited in a platinum crucible. Before it is submitted to ignition, however, it must be rendered completely dry; otherwise, it is liable to produce dust, in consequence of which, a portion of it might very easily be lost. The platinum crucible which contains the silicic acid, must, when the ignition is finished, be immediately covered with a cover which shuts close. When it has become cool, it is weighed. If the ignited silicic acid is allowed to cool in a crucible without a cover, it attracts moisture from the air quicker than most other pulverulent substances.

A variety of compounds are formed by silicic acid with other oxides. Some of these are very easily decomposed by stronger acids, while others withstand the action of the most powerful acids. The method of analysis is quite different with those compounds of silicic acid which are easily decomposed by other acids, from that of those which are not attackable by acids. A list of native compounds of silicic acid, in which those that are decomposable by acids are distinguished from those that cannot be so decomposed, has been given in the first part of this work.

Decomposition of Silicates by Acids.—The analysis of the silicates which are decomposable by acids, is much simpler than that of the other silicates. The analyst commonly employs pretty concentrated muriatic acid in the decomposition of these compounds. It is only in particular cases that nitric acid is taken for this purpose; and still seldomer that sulphuric acid is used. Although most of the siliceous compounds are capable of being decomposed by sulphuric acid, when finely pulverised and digested therewith, yet we make but little use of sulphuric acid as a solvent of silicates, because its employment is attended with a variety of disadvantages, which will hereafter be taken into consideration.—The siliceous compound to be examined, is finely pulverised without the addition of water, and, in order that a portion of it may be accurately weighed, is warmed very slightly, in a counterpoised platinum crucible, which is heated in the best manner when placed in the pipe of a heated stove. The operator must hereby be particularly careful to avoid using a heat exceeding that of boiling water, because many of these compounds contain water or other volatile constituents, which in such circumstances would in part be set at liberty. Besides this, the greater part of such compounds, when deprived by heat of their volatile constituents, are no longer capable of being dissolved by acids. The weighed portion of the pulverised compound is placed in a glass, which can be closely shut by a glass plate; it is therein mixed with muriatic acid. The different compounds of silicic acid are differently decomposed. With many, the decomposition takes place almost instantaneously; the silicic acid separates in the state of a jelly, and, if too great a quantity of muriatic acid has not been used, absorbs all the acid, and forms a swelled, gelatinous dry mass. Other compounds, though also, when in a finely pulverised state, easily decomposed by muriatic acid, give up the silicic acid in the state of powder, and form no jelly. Other silicates, again, are decomposed by muriatic acid with difficulty, and must be exposed to its action in a very finely-divided condition, and be obliged to undergo a long digestion, with the aid of heat, before the decomposition is effected.—The decomposed gelatinized compound is first treated with a little water; the silicic acid then separates in light flocks. Before filtering it from the solution, the operator must examine whether the acid has decomposed the compound completely. This is ascertained, in all cases where compounds of silicic acid are decomposed by acids, in a very simple manner: A glass rod is rubbed against the bottom and sides of the vessel; if this produce a creaking similar to that which is heard when fine sand is rubbed between two pieces of glass, it indicates that the compound is not yet fully decomposed, since the creaking is produced by the undecomposed mineral powder. It will also be found in these cases, that a heavy powder lies under the flocks of silicic acid. The liquid must then be poured off while the silicic acid is in suspension, and the undecomposed powder must be treated with a new quantity of muriatic acid. When occurring in the analysis of compounds which are easily decomposed by acids, this undecomposed powder can in most cases be held to proceed from foreign substances, enclosed in the silicate and not susceptible of decomposition by acids. In this case, the powder is repeatedly washed with water, and the lighter silicic acid is poured off with each portion of water, so that at last, the undecomposed powder remains alone in the vessel. The operation is very easy of performance, and does not require much habitude. The foreign substance is thereupon dried in the vessel, and is afterwards weighed; the weight is deducted from that of the portion of the compound submitted to analysis.

The silicic acid is filtered and washed. The water runs but slowly through the filter, yet the washing need not on that account be long continued, because in this case, the silicic acid is easily washed clean. After the washing, it is well dried, and then heated to redness in a counterpoised platinum crucible; immediately after ignition, the crucible is closed with a good-shutting cover, and is weighed with the silicic acid. In this manner, however, we do not obtain the whole of the silicic acid which was contained in the compound submitted to examination; a very small portion of it, not exceeding 1 or 1½ per cent., remains dissolved in the acid solution, and is subsequently precipitated with the other constituents of the silicate which are also still in solution.

It is a custom with some analysts, after the decomposition of a silicate by muriatic acid, to evaporate the whole mixture to dryness, and having thus expelled the excess of muriatic acid, to treat the dried mass with water, and so leave the whole of the silicic acid undissolved behind. This method, however, is in most cases inadequate to the purpose. There remains indeed, after the operation, a greater quantity of silicic acid undissolved; nevertheless, a very small portion of it redissolves, and this is particularly the case, when the dried mass, before being dissolved in water, is, as it generally must be, and as will be explained farther on, first treated with muriatic acid. Since, then, the whole of the silicic acid does not rest undissolved, but small portions of it have still to be separated in the course of the analysis, this operation of evaporating to dryness is unnecessary and ought to be avoided, not only because it is troublesome to perform but because it can very easily occasion a loss. Moreover, by the evaporation to dryness of the acid solution, it is possible totally to drive away many volatile constituents of the compound under examination. Many chemists who have analysed compounds of this kind, have entirely overlooked certain substances which were volatilized during the evaporation of the solution. The analyst should never, on this account, expose the compounds which are easily decomposable by muriatic acid, to heat, but only digest them cold. Warm digestion is employed only with substances of more difficult decomposition.

Treatment of Silicates, the Bases of which are insoluble in Muriatic Acid.—As most of the oxides which occur in combination with silicic acid, are easily soluble in muriatic acid, they are found in the acid solution which is filtered from the undissolved silicic acid. If the compound contains protoxide of lead or oxide of silver, it must be decomposed by nitric acid, and not by muriatic acid, otherwise, a great part of the chloride of lead, and all the chloride of silver, would remain undissolved with the silicic acid. The compounds, however, which, on being decomposed by acids, produce a jelly, never contain these two oxides. The protoxide of lead and oxide of silver are generally found in factitious compounds only, such, for example, as many glazes. These substances, reduced to a very finely pulverised state, can be totally decomposed by warm digestion in nitric acid.

Progress of the Analysis of Silicates, after the Separation of the Silicic Acid.—The substances remaining in the acid solution, which has been filtered from the silicic acid, are separated according to the methods which have been circumstantially described in the preceding pages. The procedure most generally followed, in the analyses of such compounds of silicic acid as occur in nature, is this: When the silicic acid has been separated, the acid solution is neutralised with ammonia, and a little ammonia is added in excess. Hereby, alumina and peroxide of iron are completely precipitated; they are accompanied by small quantities of magnesia and protoxide of manganese. These substances are separated from one another in the manner which has been described at page 62. The liquid is filtered from the precipitate, and the lime which it may contain is separated by means of oxalate of ammonia. If now, neither magnesia nor protoxide of manganese be present, the quantity of any fixed alcali can be determined by evaporating to dryness the solution which is filtered from the precipitated oxalate of lime. The dry mass afforded by the evaporation must be exposed for some time to a heat approaching to redness; whereupon the muriate of ammonia and the oxalate of ammonia volatilize, while the fixed alcali remains behind in the state of chloride. When the alcali is accompanied by magnesia, the determination of both is more difficult; it must be effected after the method which has been circumstantially described at page 29. When, however, no alcali is present, the quantity of magnesia is determined, after the separation of the lime, by treating the solution with carbonate of potash.

Separation of Silicic Acid from various Precipitates.—Here it is to be recalled to mind, that most of the substances separated in the course of this analysis contain very small quantities of silicic acid, which, if the analysis is to be accurately performed, must be separated and estimated. To this end, the different precipitates, after they have been heated to redness and weighed, are dissolved, separately, in muriatic acid. In every case, the small portion of silicic acid remains undissolved. It is filtered from the solution, carefully washed, heated to redness, and weighed. The weight is added to the weight of the silicic acid obtained in the early part of the analysis. By the solution of three or four substances, in this manner, various small quantities of silicic acid are obtained, which, on being reckoned together, produce, as we have already observed, only one, or at the highest, one and a half per cent. of the weight of the substance submitted to analysis. In analyses which are not desired to be very accurate, this portion of silicic acid is generally overlooked. The greatest quantity of silicic acid is obtained by the redissolving of magnesia, particularly when this base has been precipitated by carbonate of potash. The silicic acid so obtained often amounts to one per cent. The carbonate of potash, used to precipitate the magnesia, ought to have been carefully freed from silicic acid. By the redissolving of alumina and peroxide of iron, we obtain much less silicic acid; and the carbonate of lime, derived from the precipitated oxalate, invariably redissolves without a remainder.

Decomposition of Silicates by Fusion with Carbonate of Potash.—The analysis of the siliceous compounds, which cannot be decomposed by acids, is more difficult. The greater part undergo decomposition when they are finely pulverised and fused with carbonate of potash. The silicic acid combines with the potash and produces silicate of potash, while the substances which previously were in combination with the silicic acid are set at liberty. The mass, resulting from the fusion with carbonate of potash, can be fully decomposed by treatment with acids, There are, however, many precautionary measures to be observed in an analysis of this description. Particular care must be taken that the siliceous compound, which is to be fused with carbonate of potash, is pulverised to the greatest degree of fineness; for otherwise the risk is run of not having it completely decomposed, an accident which occurs in many cases from a neglect of this precaution. Now, in order to reduce the substance to be examined, to so exceedingly fine a powder, it is necessary to begin by breaking it into coarse grains. This can be performed in a steel mortar. It is also just as easy to wrap the substance in paper and break it with a hammer upon a hard stone or an iron plate, which renders a steel mortar unnecessary. The coarse powder is next to be pulverised in an agate mortar, or, what is better, on an agate slab, with water. When it is thought that a great part of the powder is ground sufficiently fine, the whole of it is poured into a glass, and more water is added: the mixture is stirred about with a glass rod, and then allowed to repose for some moments, that the coarse powder may fall to the bottom. The fine powder remaining suspended in the water, is poured off with the water into another glass. The coarse powder is returned to the mortar to be triturated again, and the operation just described is repeated. The powder suspended in the water is allowed to fall to the bottom; the water is then poured off, and the powder is dried. A small quantity of the substance remains suspended in the water, in a state of the finest division; this can only be obtained by the evaporation of the solution, for it cannot be separated by filtration. In most cases, when it is not necessary to reduce the substance for analysis to the very finest powder that can be produced, the operator triturates it with water in an agate mortar, then pours over it, in the mortar, a larger quantity of water, and, after it has been stirred, sucks the water with the fine powder it holds in suspension, into a glass tube open at both ends, and allows it to run thence into a glass. The coarse powder then remains at the bottom of the mortar, and can be triturated afresh.

When the triturated substance is not so hard as agate, it may very safely be concluded that it has rubbed nothing from the mortar; but when it is harder than agate, which, however, is very seldom the case, it must necessarily be concluded that it has increased in weight by the abrasion of the mortar. This is a very disagreeable circumstance, because the quantity rubbed from the agate mortar is difficult to be determined. It has been recommended, as a remedy for this evil, to weigh the coarse powder before it is triturated in the mortar, and to weigh the fine powder when the trituration is ended; it is then merely necessary to observe the increase of weight, to learn how much will have been abraded from the agate mortar. But this operation is very difficult, and can seldom be performed with accuracy. It is better to triturate the coarse powder in a little mortar which has been previously counterpoised in a balance, wherein large quantities can be weighed with accuracy. If, after the operation, the mortar weigh somewhat less than before, the difference will have arisen from the loss of agate by abrasion. As agate consists almost entirely of pure silicic acid, the operator has only subsequently to deduct the weight of the abraded agate from the weight of the silicic acid obtained in the analysis, and thereby from the weight of the silicate submitted to examination.

The operator places as much of the fine powder as it has been determined to analyse, in a little counterpoised platinum crucible, and dries or ignites it until it ceases to lose weight; when he has reached this point, he determines the weight of the powder. If the substance contains protoxide of iron, or any other oxide capable of being altered in its composition by exposure to a red heat, the powder must not be ignited before it is weighed. It can only be dried. The weighed powder is carefully shaken into a larger platinum crucible; after the transference, an exceedingly small quantity of the powder still remains in the little platinum crucible, which must afterwards be again weighed. It will generally be found, that the little crucible retains less than a grain of the powder; but, whatever the weight may be, it is to be deducted from that of the powder weighed for analysis.

The mineral powder in the large platinum crucible is now very carefully mingled with three and a half times or four times its weight of pure carbonate of potash, which must have been previously pulverised in a warm mortar. The mixing is performed with the help of a small glass rod, and must be continued until the mixture is rendered extremely intimate, and no little lumps of powder can any where be perceived; yet the operator must not be too long occupied in making this mixture, or the carbonate of potash will become moist. The powder which remains hanging about the glass rod must be carefully wiped off with a dry feather.—Instead of carbonate of potash, the carbonate of soda can be employed in this operation; yet only when the siliceous compound contains no magnesia, because the presence of soda can easily produce errors, when the quantitative determination of magnesia is to take place.

When the mixture is made, the crucible is closed with a cover, and placed among charcoal in a wind furnace. In the beginning it is best to apply a gentle fire, which must soon be increased, so that the crucible may remain exposed to a red heat for half an hour, or, indeed, for a full hour. A platinum crucible is very liable to be injured when heated to redness immediately in contact with charcoal, as it becomes bedecked, especially on the cover, with a melted mass produced by the silicic acid and oxides contained in the ashes of the charcoal, and which is difficult to be cleaned off. To provide against this evil, the platinum crucible is to be placed in a Hessian crucible, which can be closed with a cover. This Hessian crucible must have a cylindrical form, and not be of the common conical shape. This method presents also another advantage, namely, that the platinum crucible does not fall over when the fuel is burnt out.

According as the substance under examination contains more or less silicic acid, the mass in the crucible, after being treated with a certain uniform quantity of carbonate of potash, is found either completely fused, or only softened to a conglomerate. If the compound contain manganese, the mass has either a bluish green or a green colour, according to the proportion of manganese contained in the mineral. The operator inverts the crucible over a glass, and endeavours, by gently bending and pressing the sides of the crucible, to break the mass loose, and to shake it into the glass. This succeeds very well when the crucible contains a mere conglomerate; in such a case, the mass generally loosens from the crucible in a single lump. It does not answer so well, when the mixture is melted together; in that case, a great quantity of the compound remains in the crucible, in spite of the bending and pressing. This remainder must be softened by water, and transferred into the glass by washing, with as much accuracy as possible. The last portions of the fused mass which remain fixed in the crucible, notwithstanding the washing with water, must be treated with diluted muriatic acid, which easily loosens them from the crucible. It would also be possible to bring larger portions of the mass out of the crucible more easily by muriatic acid than by mere softening with water. It is necessary, however, to be very cautious in using the acid for this purpose, for, when too great a quantity is suddenly added, a strong effervescence is occasioned by the extrication of carbonic acid gas, which can very easily occasion a loss. If the fused mass contains manganese, cerium, or chromium, nothing but water must be employed to soften it in the platinum crucible, because the higher oxides of these metals disengage chlorine from the muriatic acid; in consequence of which, the platinum crucible would be liable to be corroded.

The fused mass having been washed into a glass, the liquid must be rendered acid by the addition of muriatic acid. It is necessary to perform this operation very cautiously. Care must be taken to avoid the production of too violent an effervescence, by adding the muriatic acid in very small portions. When the strong effervescence has finished, the glass is to be allowed to repose in a warm place; after undergoing a sufficiently long digestion, the whole will be decomposed. A great part of the silicic acid remains undissolved, in the state of light flocks; another portion exists in solution. It often happens, however, that all the silicic acid dissolves, when the mass is treated with muriatic acid. This is particularly the case, when a large quantity of carbonate of potash has been employed in the fusion, and when much water has been used to wash the mass from the crucible; more especially, if the compound contains but little silicic acid. It is now that the operator has the first opportunity of learning, whether the substance under examination has been completely decomposed by the fusion with carbonate of potash. To determine this point, a glass rod is rubbed against the sides and on the bottom of the glass vessel;

the presence of undecomposed powder is known by the production of a creaking sound. The acid solution, with the separated silicic acid, is evaporated to dryness; the operation can be performed in a platinum capsule, or, for want of that, in a porcelain capsule. When manganese, cerium, or chromium is present, the solution must always be evaporated in a porcelain capsule. The evaporation is allowed to take place on a sand bath, with the aid of a very gentle heat, which, especially towards the end of the operation, must be very moderate and well regulated. The bibulous paper, with which the capsule must be covered, to prevent the solution being contaminated by dust, must be very often renewed, because it very rapidly becomes destroyed by the vapours of muriatic acid which rise from the capsule. When the solution is so far evaporated, that it begins to grow thick, an extremely gentle heat must be applied, because the silicic acid which is separated in a glutinous state, if heated too strongly, very soon produces a spirting about, by which the analysis is rendered inaccurate. The evaporation may, however, be accelerated by the employment of a stronger heat, provided that, during the evaporation, the thickening mass is continually stirred with a glass rod. The application of heat is not discontinued until the evaporated mass has become completely dry. When the dried mass has become cool, it is moistened in an uniform manner with concentrated muriatic acid, and allowed to rest half an hour in that state in the cold. At the end of this time, the moistened mass is treated with water, upon which the silicic acid remains undissolved, while the other constituents of the substance, all combined with muriatic acid, form a solution with the water. It is next filtered; the silicic acid is properly washed, completely dried, heated to redness, and weighed. The muriatic acid solution, filtered from the silicic acid, is treated in the manner which has been described at page 273, when speaking of the analysis of such siliceous substances as are decomposable by acids.—The individual substances separated in the course of this analysis also contain very small portions of silicic acid, which, if the analysis is to be accurate, must be separated and weighed.

transferred into the glass by washing, with as much accuracy as possible. The last portions of the fused mass which remain fixed in the crucible, notwithstanding the washing with water, must be treated with diluted muriatic acid, which easily loosens them from the crucible. It would also be possible to bring larger portions of the mass out of the crucible more easily by muriatic acid than by mere softening with water. It is necessary, however, to be very cautious in using the acid for this purpose, for, when too great a quantity is suddenly added, a strong effervescence is occasioned by the extrication of carbonic acid gas, which can very easily occasion a loss. If the fused mass contains manganese, cerium, or chromium, nothing but water must be employed to soften it in the platinum crucible, because the higher oxides of these metals disengage chlorine from the muriatic acid; in consequence of which, the platinum crucible would be liable to be corroded.

The fused mass having been washed into a glass, the liquid must be rendered acid by the addition of muriatic acid. It is necessary to perform this operation very cautiously. Care must be taken to avoid the production of too violent an effervescence, by adding the muriatic acid in very small portions. When the strong effervescence has finished, the glass is to be allowed to repose in a warm place; after undergoing a sufficiently long digestion, the whole will be decomposed. A great part of the silicic acid remains undissolved, in the state of light flocks; another portion exists in solution. It often happens, however, that all the silicic acid dissolves, when the mass is treated with muriatic acid. This is particularly the case, when a large quantity of carbonate of potash has been employed in the fusion, and when much water has been used to wash the mass from the crucible; more especially, if the compound contains but little silicic acid. It is now that the operator has the first opportunity of learning, whether the substance under examination has been completely decomposed by the fusion with carbonate of potash. To determine this point, a glass rod is rubbed against the sides and on the bottom of the glass vessel;

the presence of undecomposed powder is known by the production of a creaking sound. The acid solution, with the separated silicic acid, is evaporated to dryness; the operation can be performed in a platinum capsule, or, for want of that, in a porcelain capsule. When manganese, cerium, or chromium is present, the solution must always be evaporated in a porcelain capsule. The evaporation is allowed to take place on a sand bath, with the aid of a very gentle heat, which, especially towards the end of the operation, must be very moderate and well regulated. The bibulous paper, with which the capsule must be covered, to prevent the solution being contaminated by dust, must be very often renewed, because it very rapidly becomes destroyed by the vapours of muriatic acid which rise from the capsule. When the solution is so far evaporated, that it begins to grow thick, an extremely gentle heat must be applied, because the silicic acid which is separated in a glutinous state, if heated too strongly, very soon produces a spirting about, by which the analysis is rendered inaccurate. The evaporation may, however, be accelerated by the employment of a stronger heat, provided that, during the evaporation, the thickening mass is continually stirred with a glass rod. The application of heat is not discontinued until the evaporated mass has become completely dry. When the dried mass has become cool, it is moistened in an uniform manner with concentrated muriatic acid, and allowed to rest half an hour in that state in the cold. At the end of this time, the moistened mass is treated with water, upon which the silicic acid remains undissolved, while the other constituents of the substance, all combined with muriatic acid, form a solution with the water. It is next filtered; the silicic acid is properly washed, completely dried, heated to redness, and weighed. The muriatic acid solution, filtered from the silicic acid, is treated in the manner which has been described at page 273, when speaking of the analysis of such siliceous substances as are decomposable by acids.—The individual substances separated in the course of this analysis also contain very small portions of silicic acid, which, if the analysis is to be accurate, must be separated and weighed.

—If the substance under examination contained protoxide of iron, that base, by the evaporation of the muriatic acid solution, will have been fully converted into peroxide of iron, on which account the addition of nitric acid is quite unnecessary, and must on other considerations be altogether avoided.

The reason that the dried mass must be moistened with muriatic acid, is, that many substances, during the evaporation, and especially towards the end, when the mass begins to become dry, and the heat is increased, that many substances in this case lose their acid, and thereupon become insoluble in water. Magnesia, alumina, and peroxide of iron, are particularly liable to lose their acid when evaporated to dryness by a strong heat, and then to become almost entirely insoluble in water. It is only when, having these substances in the dried state, the operator moistens them with muriatic acid, that they subsequently dissolve in water. If he act otherwise, if, for example, he add to the dried mass, water which has been acidulated by muriatic acid, the solution of the above-named substances is not fully effected. The silicic acid obtained in such a case, when the compound contained much peroxide of iron, would exhibit a reddish colour, in consequence of being contaminated by peroxide of iron. This is never the case, when, previous to the addition of the water, the dry mass has been treated with concentrated muriatic acid.

Analysis of Silicates which contain Alcalies.—When a siliceous substance has been decomposed by fusion with carbonate of potash, the analyst can subsequently effect, by the ordinary processes, the quantitative determination of almost all its constituents. The fixed alcalies, however, when they occur in siliceous substances, require for their quantitative determination a different procedure. In this case, when he has a sufficiently large quantity of the substance for examination, the analyst generally decomposes one portion by carbonate of potash, to determine the quantity of silicic acid and most of the other constituents, and then employs a separate portion for the determination of the fixed alcalies. Hereby, many difficulties arise in the analysis, the principal cause of which is, that by most of the methods which have been recommended for the separation of the fixed alcalies, it is impossible to obtain, with the greatest accuracy in manipulation, the proper quantity of alcali. In almost all cases, the analysis furnishes less alcali than the substance which is analysed really contains.

For the quantitative determination of the alcalies, when occurring in siliceous substances not capable of being decomposed by acids, a variety of processes have been published. We shall describe, however, only those which are actually capable, when properly conducted, of giving accurate results. For the purpose, then, of separating the alcalies, the substance to be examined may be decomposed by carbonate of barytes, by fluor spar, or by hydrofluoric acid.

Decomposition of Silicates by Carbonate of Barytes.—If the siliceous substance is to be decomposed by means of carbonate of barytes, it is necessary to commence by levigating the substance until the powder is exceedingly fine; it is required to be much finer than that which is employed in decompositions with carbonate of potash. The operator then weighs out a convenient quantity of the powder, places it in a platinum crucible, and mingles it in the most intimate manner with from 5 to 6 times its weight of very pure carbonate of barytes. This salt must, on no account, have been prepared by precipitation from the solution of a barytic salt by means of a fixed alcaline carbonate, since it might then possibly retain a portion of the fixed alcali belonging to the precipitant. When the barytic salt is prepared for this purpose, nothing but carbonate of ammonia dare be employed to precipitate it. The mixing of the siliceous powder with the carbonate of barytes must be effected with extraordinary accuracy, as it is principally upon this that the complete decomposition of the silicate depends. The compound is decomposed much more difficultly by carbonate of barytes than by carbonate of potash, and chiefly because the carbonate of potash fuses, and thereby, even when incompletely mingled, is brought into immediate contact with all parts of the siliceous powder. Hence, the compound is almost always completely decomposed when it has been fused with carbonate of potash. The carbonate of barytes does not melt, but merely forms a conglomerate with the siliceous substances it is treated with; and even this occurs only when every minute grain of the compound is encompassed with a coat of carbonate of barytes. The operator should, therefore, in the mixing, go to work with much precaution, and devote thereto at least half an hour. When the mixture is made, the platinum crucible must be exposed to a very strong heat, much stronger than that which would have been requisite had carbonate of potash been employed to effect the decomposition. When the crucible is completely cold, the mass it contains is treated in the same manner as if the substance had been fused with carbonate of potash. The conglomerated mass is transferred to a glass, and digested with muriatic acid. The acid must previously, however, have been pretty much diluted with water, and must not be added in too great an excess, because the chloride of barium which is formed by the operation, is very sparingly soluble in muriatic acid, especially when the acid has not been diluted with a large proportion of water. When the acid has effected the decomposition of the heated mass, the operator must carefully examine whether any undecomposed powder remains. This is found to be the case very often, when the mixture of the substance with the carbonate of barytes has not been rendered extremely intimate. When undecomposed powder is discovered to be present, it is almost the best plan, if the operator possess a sufficient quantity of the substance to be examined, to commence a new analysis. If he does not choose to begin anew, he must endeavour to separate, by washing, the light flocky silicic acid from the heavy undecomposed powder; he must then determine the weight of the undecomposed mass, and deduct it from the weight of the substance submitted to experiment. The quantity of silicic acid which is separated in flocks when the decomposition has been effected by carbonate of barytes, is greater than that produced when carbonate of potash is employed as the decomposing agent; still, however, there always remains a considerable quantity of silicic acid dissolved in the acid solution. In order to separate this, it is necessary to proceed in the manner which has been described at page 279. The solution must be evaporated to perfect dryness. The dried mass must be moistened with muriatic acid, and left for half an hour to itself, that the muriatic acid may have full opportunity to act upon it. Water is then to be added to dissolve the soluble salts. The silicic acid remains undissolved. The operator should never neglect to determine the weight of this silicic acid, even though the proportion of silicic acid contained in the compound under examination may have been previously determined by another analysis through decomposition with carbonate of potash. If the weight of the silicic acid obtained by both processes be the same, it is a proof that the decomposition of the compound has been as completely effected by the carbonate of barytes as by the carbonate of potash.

The barytes contained in the muriatic acid solution filtered from the silicic acid, is precipitated by sulphuric acid, as sulphate of barytes. The addition of a great excess of sulphuric acid must be avoided. The greater the accuracy with which the barytes is saturated, and the less the excess of sulphuric acid left in the solution, the easier and the more exact will be the subsequent determination of the quantity of the alcali. The great mass of sulphate of barytes thus precipitated must be carefully washed; when the substance under examination contains a considerable quantity of lime, the washing of the sulphate of barytes must be long continued. If the quantity of lime is extremely large, it is customary, not to continue the washing of the sulphate of barytes till all the lime is washed away, but to wash it only till it be supposed to be free from all the alcaline sulphate. The filtered solution is then commonly mixed with caustic ammonia, which precipitates alumina and peroxide of iron. It is advisable to determine separately the quantities of these two substances, and to compare them with those which have been furnished by the other analysis in which the substance was decomposed by carbonate of potash. The sulphate of lime which the filtered liquor may contain is precipitated by oxalate of ammonia.

If, now, neither magnesia nor protoxide of manganese, nor, indeed, besides the alcalies, any constituents unprecipitable or partially unprecipitable by ammonia remain present, then the solution which has been filtered from the oxalate of lime contains, as fixed constituents, only the alcalies that are sought for, and those alcalies in the state of sulphates. The solution is evaporated to dryness, and the dry mass is heated to redness; hereupon, the ammoniacal salts volatilize, and acid sulphates of alcalies remain behind. In the ignition of the dry mass, the greatest precaution must be employed, because it is in this particular operation that the greatest loss of alcali can be occasioned. The dry mass, in addition to the fixed alcaline sulphates, contains sulphate and muriate of ammonia; and when lime has been precipitated, oxalate of ammonia. When this mass of compounds is ignited, the muriate of ammonia flies away; the small quantity of oxalate of ammonia is first changed into carbonate of ammonia, and then driven away; and no loss can be produced by either of these. But the sulphate of ammonia melts when heated, and soon begins to boil, whereupon it commonly spirts about pretty strongly, and can easily occasion a loss of part of the fixed alcali. The smaller the excess of sulphuric acid added to precipitate the barytes, the easier is the expulsion of the ammoniacal salts effected; because, in that case, the quantity of the sulphate of ammonia is so much the smaller. To ignite the dry mass, it is best to place it at first in a roomy platinum capsule, because in this utensil the least loss can be occasioned by any spirting about. When nearly all the volatile salts are driven away, the remainder is washed with water into a small counterpoised platinum capsule or crucible, and then evaporated to dryness, and ignited. As, however, the remainder consists of acid sulphate of alcali, it is necessary to add solid carbonate of ammonia during the ignition of the mass; a neutral alcaline sulphate is then obtained, from the weight of which the quantity of alcali is calculated.

When the substance under examination contains magnesia as well as an alcali, the estimation of the alcali becomes still more difficult, and is attended with yet more loss. In this case, to the solution which has been filtered from the oxalate of lime, and which then contains no other fixed constituents than magnesia and the alcali, the solution of the very small quantity of magnesia, which had previously been precipitated by ammonia, is added. Thereupon, the mixture is evaporated to dryness, the common weight of the sulphate of alcali and sulphate of magnesia is determined, and the two salts are then separated by a solution of acetate of barytes, the method of doing which has been already explained at page 29.

As it is so difficult to determine with accuracy the quantity of fixed alcaline sulphates, when sulphate of ammonia is present, a process altogether different is often resorted to, when such substances fall to be analysed. The muriatic acid solution, which has been filtered from the silicic acid; is mixed with carbonate of ammonia. This produces a precipitate of carbonate of barytes, with alumina, peroxide, of iron, &c. The solution is filtered and evaporated to dryness, and the dry mass is ignited. The alcali is then obtained in the state of a metallic chloride. This method, however, gives no accurate result. As there is a pretty large quantity of carbonate of barytes, which is not quite insoluble in water, there is always a greater or lesser portion of this substance dissolved during the washing of the precipitate. The dissolved carbonate of barytes is converted into chloride of barium by the sal ammoniac in the solution, and, in the end, the metallic chloride produced by the alcali is always accompanied by chloride of barium.

Decomposition of Silicates by Nitrate of Barytes.—Instead of carbonate of barytes, chemists formerly employed nitrate of barytes, to effect the decomposition of minerals containing alcalies. But the use of nitrate of barytes is accompanied by more difficulties. It is decomposed when ignited, and the pure barytes which results, works alone the decomposition of the silicate which it is fused with. As caustic barytes, however, when heated very powerfully, injures the platinum crucible, it is necessary to effect the decomposition in a silver crucible, which supports, unfortunately, no very strong degree of heat. When, farther, the operator has succeeded, by soaking and washing with water, in bringing the greater part of the ignited mass out of the crucible, and would willingly employ muriatic acid to loosen it completely from the sides of the crucible, he dare not do so, unless he submit to have chloride of silver among the insoluble silicic acid. But the most disagreeable circumstance attending this decomposition is, that the nitrate of barytes, when decomposed by heat, rises with extraordinary facility above the edges of the crucible. The best way to hinder this is to proceed as follows: The pulverised nitrate of barytes, which must have been previously so strongly heated that it can no longer decrepitate, is mixed with the substance to be examined, and the mixture, in a silver crucible, is exposed to the heat of a spirit lamp with circular wick. The heat must at first be very gentle, but be gradually increased and kept up till the rising of the mass in the crucible ceases; till, in short, the nitrate of barytes is almost completely decomposed. The crucible is then placed among charcoal and exposed to the strongest degree of heat which the silver can support without melting. When the mass is cold, it is treated exactly in the same way as it would have been, if, instead of nitrate of barytes, the carbonate of barytes had been used to decompose it.—As the nitrate of barytes fuses, it can more easily effect the full decomposition of the substance submitted to analysis, the more especially that the caustic barytes produced by the ignition acts much more powerfully than the carbonate; yet this method is advantageously employed only with such substances as cannot be finely pulverised, as mica; or with substances which withstand the action of carbonate of barytes.

Decomposition of Silicates by Fluor Spar.—There is another method of quantitatively determining the quantity of fixed alcali contained in the siliceous substances which cannot be decomposed by acids. The decomposing agent employed in this method, which was first recommended by BERZELIUS, is fluor spar. The course of the analysis is as follows: One part of the siliceous substance, obtained by levigation and washing in a state of fine division, is mingled with about five parts of fluor spar, which must be free from every metallic admixture. It is unnecessary to levigate the fluor spar. It need only be finely pulverised. The mixture must be very intimate, and must be made in a platinum capsule, or in a large platinum crucible. The operator mixes with this powder, with the help of a platinum spatula, as much concentrated oil of vitriol as is sufficient to make the mass into a pap. The platinum capsule is then gradually warmed, upon which there is a disengagement of hydrofluoric gas and fluosilicic gas. The temperature is increased until the platinum vessel is exposed to a dull red heat, which ensures the expulsion of the excess of sulphuric acid. In this case, the silicic acid of the substance under examination is volatilized with the fluorine of the fluor spar. When alumina is present, it combines at first with the sulphuric acid, but the subsequent exposure to a dull red heat expels a portion of the sulphuric acid; on which account, when the mass is afterwards treated with water, the greater part of the alumina remains undissolved. It being, however, often of importance to determine the quantity of alumina, it is necessary to adopt the following process. When the mixture has been gently ignited to drive away the free sulphuric acid, the mass is moistened in an uniform manner with concentrated muriatic acid. The whole is left in this state to act in the cold, for an hour, or still longer. The mixture is then washed with water into a glass, more water is added to it, and it is exposed for some time to a warm digestion. What remains undissolved, at the end of this process, consists chiefly of sulphate of lime. It is filtered and washed. In order to determine whether the insoluble substance be sufficiently washed or not, a portion of the water which has last passed through the filter is tested with liquid ammonia. If a precipitate of alumina is formed, the washing must be continued, and can only be considered as complete when ammonia, applied as above, no longer produces a precipitate. Of course, when alumina was not contained in the substance submitted to analysis, this [illegible] of testing the accuracy of the washing is ineffectual.

The tested portions of the wash-water must not be thrown away, but must be added to the filtered muriatic acid solution. The operator then supersaturates this solution with ammonia, and filters it from the precipitate as quickly as possible. This haste is required to prevent the contamination of the precipitate by carbonate of lime; yet, on account of the great quantity of sulphate of lime in solution, and of the unavoidable excess of ammonia, it is difficult to prevent the formation of carbonate of lime. The precipitate contains the whole quantity of alumina and peroxide of iron; the proportion of each is to be determined, in order that the quantities may be compared with those obtained in the other analysis, in which the same substance was decomposed by carbonate of potash. It is, however, necessary to observe here, that the precipitate contains almost always a trace of lime. From the filtered solution, the lime of the dissolved sulphate of lime is precipitated by oxalate of ammonia. The solution, separated from the oxalate of lime, is evaporated to dryness, and the dry mass produced is heated to redness. The substance which remains is the alcali of the mineral, in the state of bisulphate. It is reduced to the state of neutral sulphate, by ignition with dry carbonate of ammonia. The ignition of the dry mass is, in this analysis, accompanied by few difficulties, because the quantity of sulphate of ammonia is commonly not so considerable as it is when the siliceous substance has been treated with carbonate or nitrate of barytes.

Decomposition of Silicates by Hydrofluoric Acid.—If the operator is in possession of a platinum retort, he may decompose the siliceous substances which contain alcalies and are incapable of decomposition by common acids, by means of hydrofluoric acid. The employment of hydrofluoric acid has very many advantages over that of fluor spar, since, with the exception of the silicic acid, all the constituents of the substance, even the lime, can be determined. This method, which, as well as the preceding, was first recommended by BERZELIUS, gives the most accurate result of all, and that, too, in a far shorter time than when the substance is treated with fluor spar; because the wash-

of the great mass of sulphate of lime which is pro-
ced when fluor spar is employed, occupies a very long
e. It is necessary, however, to prepare for every ana-
is a fresh portion of right concentrated hydrofluoric
id, for this acid soon loses its strength, and is incapable
preservation in a state fit for action. To prepare the
drofluoric acid, the operator takes pulverised fluor spar,
ich must be quite free from metallic admixture and
rticularly from copper pyrites. He places the powder in
under part of the retort, the upper part of which should
so contrived as to be capable of removal. He adds so
ch concentrated sulphuric acid, that when the whole is
xed together with a platinum spatula, it produces a
ck pap. He then fixes the upper part of the retort upon
under part, and leads the neck into a platinum crucible
ich contains a little water. The neck of the retort must
ter the water in such a manner that the orifice is partly
ove and partly below the surface of the liquid. The
id is distilled over by the gentle heat of a small spirit
np. The operation is continued until the aqueous acid
the platinum crucible, after separation from the retort,
ongly smokes; for it is only from the employment of a
ning acid that the operator can expect the complete
composition of the siliceous substance submitted to
alysis. Over the substance, previously very finely pul-
rised and weighed, the operator gradually pours this
ning acid. The operation is best performed in a roomy
tinum capsule, because the action is so violent, that the
id generally boils and causes a spirting about, which,
re the operation to be performed in a small platinum
sel, might occasion a loss. The mixture is repeatedly
rred with a platinum spatula, and sulphuric acid is then
tiously added to it; after this, the whole is evaporated
dryness, the heat first applied being very gentle, and
n gradually raised higher. There takes place, at the
ginning, a discharge of fluosilicic gas and hydrofluoric
s; the excess of sulphuric acid goes away only at an
reased temperature; its entire expulsion is not effected
til the bottom of the platinum capsule is heated to dull
ness. When all is cold, the dry mass is moistened with

concentrated muriatic acid; and when this has had sufficient time to operate, water is added to the mixture, and every thing but a small quantity of silicic acid is dissolved. The solution is filtered. The silicic acid very often runs with the solution through the filter; but if the solution be previously warmed, the filtration is effectual in separating the silicic acid. The filtered muriatic acid solution contains all the constituents of the substance under examination, with the exception of the silicic acid. The separation of the various substances is effected by the processes which have been already often described. When lime is contained in the substance, the quantity of it can be perfectly well determined; but, as the sulphate of lime is difficultly soluble in water, care must be taken to wash the insoluble silicic acid on the filter, until the sulphate of lime is completely separated.—The alcali can, by this method, be very well and very accurately estimated, since, in all cases, the quantity of sulphate of ammonia, which is to be expelled from the sulphate of fixed alcali, must necessarily be very small.—All siliceous substances cannot, however, be completely decomposed by hydrofluoric acid. The imperfect decomposition of a substance is immediately discerned, when, upon pouring the fuming hydrofluoric acid over it, no violent action, and no very strong degree of heat, is produced. There is reason to believe that the substances which withstand the decomposing action of carbonate of potash, withstand also the decomposing action of hydrofluoric acid. If it be desired to determine the quantity of fixed alcali in such substances as are indecomposable by hydrofluoric acid, the most advisable process is decomposition by nitrate of barytes.

It is not allowable, in the preparation of hydrofluoric acid for such analyses, to employ a retort of lead instead of platinum; for, with a retort of lead, the operator would be sure of obtaining an acid holding protoxide of lead in solution.

Decomposition of Silicates by Caustic Potash.—We have still to treat of the analysis of the siliceous substances which withstand the decomposing action of the carbonate of potash. Of the compounds which occur in nature, very few are of this description. They are characterised by an extreme degree of hardness, on which account difficulties arise even in the pulverising of the substances, since it is troublesome to determine the exact quantity of silica which is abraded from the agate mortar, by the substance pulverised. We have already, at page 275, spoken of the manner in which this difficulty is best overcome. But as nearly all these very hard substances appear to be indecomposable by liquid hydrofluoric acid, the operator can also employ a dilute, and not fuming hydrofluoric acid to dissolve the powder which is abraded from the mortar, and which may be considered as pure silicic acid. The substance to be examined then remains behind in a state of purity. The dry powder when removed from the mortar is placed in a platinum capsule, hydrofluoric acid is poured over it, the mixture is stirred with a platinum spatula, the undissolved powder is allowed to fall down, and the liquid is then poured off. The powder is then washed with water, and the washing is continued until the liquid which is poured off ceases to affect the colour of blue bitmus paper. The powder is then dried.—For the decomposition of these substances caustic potash is employed, the use of which, however, is attended by a great many difficulties. In general; it is not dry caustic potash which is employed; but, after having placed the finely pulverised mineral in a large silver crucible, a concentrated solution of caustic potash of a determined strength is poured over it. The whole is then evaporated to dryness, the mixture being continually stirred with a silver spatula: the dry mass is then heated to redness. This operation can be effected only in a silver crucible, because a platinum crucible would be strongly acted upon by the caustic potash. During the ignition the mass spirts about: on this account, a very gentle heat must be employed at first, and it must be increased gradually. When the boiling is at an end, the mass is exposed to the strongest degree of heat which the silver crucible can support without melting. After the ignition, another difficulty is found in bringing the mass out of the crucible: it sticks to the sides of the vessel, and if muriatic acid is used to loosen it, the silicic acid which is obtained is found to be mingled with chloride of silver. These great disadvantages accompanying the employment of caustic potash are avoided in a process successfully practised by BERZELIUS (POGGENDORFF'S Annalen, B. IV. p. 132). This process is as follows: The ignited and weighed powder of the substance to be analysed is mingled, in a platinum crucible, with three times its weight of carbonate of potash or carbonate of soda, and a cavity is formed in the middle of the mass. Thereupon, the crucible is gently ignited for a quarter of an hour, but the mixture is not permitted to melt. It is then allowed to cool. The operator now places in the cavity rather more than one part of caustic potash or caustic soda, and again slowly heats the crucible. Hereupon the caustic alcali gradually sinks into the porous mass, and causes no spirting about, as it generally does when it gives up its water. The heat is then so much increased that the crucible becomes white hot. The platinum crucible is not injured thereby. The ignited mass is afterwards treated in the same manner as it would have been had the mineral been decomposed by carbonate of potash alone.

Estimation of the Water contained in Silicates.—Many of the siliceous substances which occur in nature, and which are decomposable by muriatic acid, contain water. The quantity of the water is determined, in most cases, by the loss of weight which is suffered when a given quantity of the compound is heated to redness in a small platinum crucible. The ignition, however, deprives the siliceous compound of the property of being decomposable by muriatic acid; its farther analysis therefore must be undertaken with another portion. If, however, the operator possess so small a quantity of the compound that he can only undertake a single analysis for the determination of all the constituents, if, for example, he possess no more than 20 or 30 grains, then, after the estimation of the water, he must decompose the compound by fusion with carbonate of potash.

Examination of the Purity of the Silicic Acid.—The operator must never neglect to examine the purity of the silicic acid which he may obtain by any one of the above-cited processes. The examination of the silicic acid is particularly necessary in the analysis of the minerals which carbonate of potash does not easily decompose. He should try the purity of every distinct portion of silicic acid he obtains, especially of the small portions procured by dissolving the different precipitates in muriatic acid. The proof consists in fusing a small quantity of the silicic acid with soda, on charcoal, before the blowpipe. If a transparent colourless glass is produced, the silicic acid is either quite pure, or at any rate contains no great quantity of foreign matters. In the analysis of such siliceous substances as are easily decomposable by carbonate of potash, the operator may generally content himself with this proof, as the silicic acid then obtained is almost always pure. But when the substance is difficult of decomposition, and can only be decomposed by caustic potash, the silicic acid which is obtained must be much more carefully examined. The silicic acid can in this case contain a considerable quantity of alumina, a substance of which the above test does not readily intimate the presence. The quantity of alumina contained in the silicic acid may be pretty considerable, may amount to 12 or 15 per cent. of the weight of the silicic acid, and still the glass formed by the fusion of this mixture with soda may remain transparent. The operator must never neglect to submit the silicic acid, obtained under the above-named circumstances, to a full analysis. A portion of the silicic acid must be fused with a considerable quantity of carbonate of potash, the melted mass must be treated with muriatic acid, and the solution must be evaporated to dryness. The dry mass must then be moistened with muriatic acid, and afterwards treated with water. The muriatic acid solution, filtered from the undissolved silicic acid, must now be supersaturated with ammonia. If the solution give no precipitate, the silicic acid may be considered to have been pure; but if a precipitate is formed, this can only arise from the foreign matters with which the silicic acid was combined. In most cases, the precipitate is alumina; for it is in consequence of the presence of an extremely large proportion of alumina in siliceous substances that the latter are often imperfectly decomposed by carbonated, and even by caustic potash.

By the methods which have been described in the preceding pages, the separation of silicic acid from most bases, is easily effected. As nearly all the bases with which silicic acid occurs in combination are soluble in muriatic acid, they are, of course, always contained in the muriatic acid solution filtered from the silicic acid. When the base is one of those which are insoluble in muriatic acid, such as oxide of silver or protoxide of lead, the operator, as it has been already remarked, instead of muriatic acid, employs nitric acid for the analysis. There are, however, in the separation of silicic acid from some few bases, a variety of particular precautions to be observed. We shall now proceed to the consideration of these cases.

Separation from Phosphoric Acid.—If a siliceous substance contains phosphoric acid, and is decomposed by muriatic acid, then the whole quantity of the phosphoric acid and of the bases which were combined with the phosphoric and silicic acids, are contained in the muriatic acid solution which is filtered from the undissolved silicic acid. These bases are separated from the phosphoric acid, after methods which have been described in the foregoing sections. It is better, however, to mix the siliceous substance immediately with three or four parts of carbonate of potash in a platinum crucible, and therewith to ignite it. If the siliceous substance be not decomposable by muriatic acid, then, having been pulverised and washed, it must in every case be treated in this manner. Water is poured over the ignited mass, and the insoluble portion is filtered and washed. In this case, the solution contains phosphoric acid combined with potash. It also contains the excess of carbonate of potash. The insoluble matter consists of silicic acid, and the bases which were contained in the substance submitted to analysis. The separation thus effected, is, however, not quite complete: the solution retains a small quantity of silicate of potash. The operator adds therefore a little carbonate of ammonia to the solution, and exposes it to a slight evaporation, upon which flocks of silicic acid are deposited. This silicic acid is filtered, washed, and added to the mass which was left undissolved by the watery solution. Muriatic acid is poured over the insoluble remainder; upon which an immediate decomposition takes place, and gelatinous silicic acid is deposited. That the whole quantity of silicic acid may be obtained the solution is evaporated to perfect dryness; a capsule of platinum or porcelain being employed. This operation renders the silicic acid insoluble. The dry mass is moistened in an uniform manner with muriatic acid, and after some time is treated with water. The insoluble silicic acid is separated by filtration, and the bases are precipitated from the filtered solution.—In this operation, it is best to filter the mass which is insoluble in water, upon the smallest possible filter, and after it has been washed with water, to place it, filter and all, in the muriatic acid, for it is difficult, even after the most complete drying, to separate the mass from the filter without loss. The silicic acid then obtained, is, it is true, rendered black by ignition, in consequence of the presence of charcoal; yet its white colour can be restored, if the ignition is somewhat long continued and the air is allowed free access.

It remains, in this case, to determine the quantity of the phosphoric acid. The solution filtered from the insoluble matter, is supersaturated with muriatic acid. This must be performed with care, that no loss may be occasioned by the production of too violent an effervescence. Too great an excess of muriatic acid is also to be avoided. The saturation is best effected in a shallow capsule of platinum or porcelain. The acid solution is then allowed to remain undisturbed, merely covered with filtering paper, for twenty-four hours; at the end of this time the free carbonic acid is disengaged from the solution. For the sake of greater certainty, the solution can afterwards be heated, or even boiled for some time. When this is done, the solution is poured into a flask which can be closed air-tight with a cork; an excess of ammonia is then added, and immediately afterwards a solution of chloride of calcium: the flask is then corked. In this manner, the phosphoric acid is precipitated as phosphate of lime. The flask is permitted to rest undisturbed, until the precipitate has completely subsided; the supernatant fluid is then filtered as quickly as possible, and the precipitate is brought upon the filter, and quickly washed. The keeping off the atmospheric air during the precipitation of the phosphate of lime, and the quick washing of the precipitate, are to prevent the formation of carbonate of lime. When the phosphate of lime is well dried, it is ignited and weighed; it is then decomposed by sulphuric acid. alcohol is added to the solution, and the sulphate of lime is filtered. When the weight of the sulphate of lime is known, the quantity of dry phosphoric acid by which the lime was previously saturated can be calculated.

When the substance for analysis contains phosphoric acid, with a large quantity of alumina, and only a small quantity of silicic acid, it is proper, before that substance is exposed to heat with carbonate of potash, to add to it so much silicic acid that the ignited mass may contain about one and a half parts of silicic acid to two parts of phosphate of alumina. The silicic acid must, previously to its addition to the mineral, be ignited in a covered platinum crucible, and upon becoming sufficiently cool, be very accurately weighed. The weight is afterwards to be deducted from that of the whole quantity of silicic acid furnished by the analysis.

Separation from Sulphuric Acid.—When the siliceous compound submitted to analysis contains sulphuric acid, and the compound, after being pulverised, is decomposed by muriatic acid, then the whole of the sulphuric acid is contained in the solution filtered from the silicic acid. The sulphuric acid is precipitated by a solution of chloride of barium, and its quantity is, in the usual manner, estimated from the weight of the sulphate of barytes. The excess of barytes is next precipitated from the filtered solution, as sulphate of barytes, and the quantities of the bases which existed in the compound can then be determined.

If the siliceous substance which contains sulphuric acid be indecomposable by muriatic acid, it must be reduced to a fine powder by levigation and washing, and in that state be ignited with carbonate of potash or of soda. The ignited mass is then treated with water, which dissolves both the sulphate of alcali thus formed, and the excess of carbonate of alcali. The solution is cautiously acidulated by muriatic acid, and the sulphuric acid is precipitated by a solution of chloride of barium. The mass which remained undissolved by the water, is then decomposed by muriatic acid. Generally speaking, the same precautionary measures are to be observed in the performance of this analysis, as must be observed in the examination of such siliceous substances as contain phosphoric acid. These precautions have been mentioned above.

Separation from Sulphur or Sulphurets.—If a siliceous substance which is to be analysed, contains sulphur combined with a metal, and forming a metallic sulphuret, which, for example, is the case with the native compound the Helvine, and if farther, this siliceous compound is decomposable by acids, then the best method of proceeding is, that of finely pulverising the compound, and treating it with fuming nitric acid. By this operation, all the sulphur is converted into sulphuric acid. The silicic acid is then separated by the filter, and the analysis is carried on in the manner which has been described above. C. G. GMELIN employed this method in his analysis of the Helvine. (POGGENDORFF's Annalen, B. III. p. 58).

Separation from Oxide of Chromium.—If a siliceous substance contains oxide of chromium, and if, at the same time, it is easily decomposable by muriatic acid, the analysis is accompanied by no difficulties. The oxide of chromium is found, with the other bases, in the solution filtered from the silicic acid. It is separated from these bases by methods which have been described in the preceding pages. But if the compound be not decomposable by muriatic acid, it must be fused, in the ordinary manner, with carbonate of potash in a platinum crucible. The ignited mass is afterwards transferred to a glass, and supersaturated with muriatic acid; those precautions being taken which have repeatedly been alluded to. The whole is then warmed, whereby the chromic acid formed during the ignition is reduced to oxide of chromium. To hasten the reduction, it is good to add a little alcohol to the muriatic acid. Then, however, the silicic acid which is separated in the usual way, is impure. According to TROLLE-WACHTMEISTER (*Vetenskaps Academiens Handlingar*, 1825, p. 217), it is not white, but coloured dark brown by chromium. To obtain the silicic acid in a state of purity, the analyst ignites it in a silver crucible with caustic potash, then treats the ignited mass with muriatic acid and alcohol, evaporates the whole to dryness, and moistens the dry mass with muriatic acid; after some time, he adds a quantity of water, and pure silicic acid remains undissolved. The solution, filtered from the silicic acid, contains oxide of chromium, and must be added to the solution of oxide of chromium obtained before. In the subsequent steps of the analysis, the oxide of chromium is precipitated in company with peroxide of iron or with alumina, and is separated from these substances by the process described at page 193.

Separation from Titanic Acid.—Many difficulties attend the separation of silicic acid from titanic acid. If the compound which contains both substances is of such a kind, that it can be decomposed by muriatic acid, then it is digested with that acid, being first finely powdered, or in case of necessity, reduced to the finest state of division by levigation and washing. But the digestion must be effected in the cold, or at any rate must be supported by so gentle a degree of heat that the titanic acid be not precipitated; for, if once that acid be deposited, it does not again dissolve in any excess of muriatic acid. When the compound is completely decomposed, the undissolved silicic acid is filtered, dried, and weighed. From the filtered solution, the titanic acid is precipitated by ammonia. The small quantity of silicic acid which, in company with the titanic acid, is held in solution by the muriatic acid, cannot, by this method, be estimated; it is, however, extremely small, and cannot amount to one per cent.—In this separation, it is necessary to observe the precaution of washing the silicic acid with cold and not with hot water. Particular care must, moreover, be taken, that during the digestion of the substance with muriatic acid, the heat applied remain as gentle as possible.

More difficult is the separation of silicic acid from titanic acid, when they occur together in compounds, which other acids are incapable of decomposing. The best method to adopt in this case is the following: To fuse the finely levigated compound with carbonate of potash or carbonate of soda, in a platinum crucible. To pour an excess of diluted muriatic acid over the fused mass, and dilute the solution with water. The action of the acid in the fused substance must not be assisted by heat. Flocks of silicic acid remain undissolved; the greater or smaller quantity of which depends on the greater or smaller quantity of the carbonate of alcali with which the compound has been fused, and on the greater or more inconsiderable dilution of the acid employed to dissolve it. The titanic acid is completely dissolved. The solution is filtered from the insoluble silicic acid, and the latter is washed with cold water. The solution is then supersaturated with ammonia, by which the titanic acid is precipitated in company with the silicic acid. The precipitate is filtered, and washed with cold water. It is then allowed to become perfectly dry: the drying, however, must be effected by the air alone, and not by placing the precipitate in a warm situation. When the precipitate is perfectly dry, it is digested in concentrated muriatic acid, without heat; thereupon, the titanic is dissolved, while the silicic acid remains undissolved. The latter is separated by filtration, and from the filtered liquid the titanic acid is precipitated by ammonia; the precipitated titanic acid is dried, ignited, and weighed.—The solution, filtered from the double precipitate of titanic and silicic acids, contains still a small quantity of silicic acid, in addition to all those constituents of the substance which ammonia is incapable of precipitating. To separate the silicic acid, the solution is supersaturated with muriatic acid, and then evaporated to dryness.

When the compound to be analysed contains constituents which ammonia is incapable of precipitating in company with the titanic acid; when, for example, it contains peroxide of iron, the examination becomes still more difficult. These substances dissolve, with the titanic acid, in muriatic acid. The constituents of the solution so formed, can be separated by the process described at page 170.

Separation from Peroxide of Tin.—It happens very frequently, that siliceous compounds contain small quantities of peroxide of tin. When these substances are indecomposable by muriatic acid, and must, on that account, be decomposed by treatment with carbonate of alcali, it is often found that the silicic acid then separated contains a small quantity of peroxide of tin. The peroxide of tin is, in that case, sometimes combined with an earth, and especially with glucina, when glucina is a constituent of the substance submitted to analysis. This small portion of peroxide of tin is very easily obtained by digesting the silicic acid, previously to its ignition, with bihydrosulphuret of ammonia: the tin is then dissolved. The digestion is best performed as follows: The neck of the funnel upon which the silicic acid has been filtered, and upon which it still remains, is pretty thickly smeared with tallow, and is then fixed into the mouth of a small flask in such a manner as to close the flask air-tight. Bihydrosulphuret of ammonia is then poured over the silicic acid, with which, not being able to flow away, it remains very long in contact. When it is thought that all the tin is dissolved, the funnel is freed from the flask, and the liquid allowed to descend. The solution of tin is evaporated to dryness, and the dry mass is strongly ignited; the small quantity of sulphuret of tin is then converted into pure peroxide of tin.—With respect to the peroxide of tin which may have been dissolved by the muriatic acid, at an early stage of the analysis, the best way to separate it, is to pass a stream of sulphuretted hydrogen gas through the acid solution filtered from the silicic acid; a small precipitate of sulphuret of tin in then obtained, which upon being ignited, yields peroxide of tin.—BERZELIUS has detected small quantities of peroxide of tin in several minerals, namely, in Smaragdite, Euclase, and others.

Separation from Deutoxide of Copper.—If a siliceous substance contain deutoxide of copper, it is best, after the separation of the silicic acid, to precipitate the copper from the acid solution, by a stream of sulphuretted hydrogen gas. The sulphuret of copper is afterwards to be treated in the manner described at page 111. When the quantity of deutoxide of copper contained in a substance is extremely small, as it is, for example, in the cupreous Idocrase from Norway, it is often very easy to miss it altogether, by neglecting to precipitate it immediately after the separation of the silicic acid.

Separation from the Oxides of Iron.—It has been already mentioned, at page 72, that it is quite impossible to determine the respective quantities of peroxide of iron and protoxide of iron, contained in a substance which cannot be decomposed by muriatic acid. This is the case with the siliceous compounds which contain both the oxides, and which have to be decomposed by treatment with carbonated or caustic alcali. When, however, the two oxides occur in a siliceous compound which is decomposable by muriatic acid, as, for example, is the case with the mineral called Ilvait or Lievrite, the proportion of the oxides can be determined by the following method: A portion of the compound is placed in a flask which can be closed air-tight, and is treated with muriatic acid in the manner described at page 69. When the decomposition of the compound is fully effected, and every thing but the silicic acid is dissolved, liquid sulphuretted hydrogen is added to the solution. After some days, when the solution has become clear, the mixture of silicic acid and sulphur is separated by filtration, and washed. It is then permitted to become perfectly dry, and is afterwards cautiously treated with nitric acid, by which the sulphur is completely converted into sulphuric acid. The silicic acid is separated by filtration, and the sulphuric acid is precipitated from the liquid, by a solution of chloride of barium. It is necessary to treat the silicic acid a second time with fuming nitric acid, to ascertain whether it be altogether free from sulphur. From the weight of the sulphate of barytes, the quantity of precipitated sulphur company with the titanic acid; when, for example, it contains peroxide of iron, the examination becomes still more difficult. These substances dissolve, with the titanic acid, in muriatic acid. The constituents of the solution so formed, can be separated by the process described at page 170.

Separation from Peroxide of Tin.—It happens very frequently, that siliceous compounds contain small quantities of peroxide of tin. When these substances are indecomposable by muriatic acid, and must, on that account, be decomposed by treatment with carbonate of alcali, it is often found that the silicic acid then separated contains a small quantity of peroxide of tin. The peroxide of tin is, in that case, sometimes combined with an earth, and especially with glucina, when glucina is a constituent of the substance submitted to analysis. This small portion of peroxide of tin is very easily obtained by digesting the silicic acid, previously to its ignition, with bihydrosulphuret of ammonia: the tin is then dissolved. The digestion is best performed as follows: The neck of the funnel upon which the silicic acid has been filtered, and upon which it still remains, is pretty thickly smeared with tallow, and is then fixed into the mouth of a small flask in such a manner as to close the flask air-tight. Bihydrosulphuret of ammonia is then poured over the silicic acid, with which, not being able to flow away, it remains very long in contact. When it is thought that all the tin is dissolved, the funnel is freed from the flask, and the liquid allowed to descend. The solution of tin is evaporated to dryness, and the dry mass is strongly ignited; the small quantity of sulphuret of tin is then converted into pure peroxide of tin.—With respect to the peroxide of tin which may have been dissolved by the muriatic acid, at an early stage of the analysis, the best way to separate it, is to pass a stream of sulphuretted hydrogen gas through the acid solution filtered from the silicic acid; a small precipitate of sulphuret of tin in then obtained, which upon being ignited, yields peroxide of tin.—BERZELIUS has detected small quantities of peroxide of tin in several minerals, namely, in Smaragdite, Euclase, and others.

Separation from Deutoxide of Copper.—If a siliceous substance contain deutoxide of copper, it is best, after the separation of the silicic acid, to precipitate the copper from the acid solution, by a stream of sulphuretted hydrogen gas. The sulphuret of copper is afterwards to be treated in the manner described at page 111. When the quantity of deutoxide of copper contained in a substance is extremely small, as it is, for example, in the cupreous Idocrase from Norway, it is often very easy to miss it altogether, by neglecting to precipitate it immediately after the separation of the silicic acid.

Separation from the Oxides of Iron.—It has been already mentioned, at page 72, that it is quite impossible to determine the respective quantities of peroxide of iron and protoxide of iron, contained in a substance which cannot be decomposed by muriatic acid. This is the case with the siliceous compounds which contain both the oxides, and which have to be decomposed by treatment with carbonated or caustic alcali. When, however, the two oxides occur in a siliceous compound which is decomposable by muriatic acid, as, for example, is the case with the mineral called Ilvait or Lievrite, the proportion of the oxides can be determined by the following method: A portion of the compound is placed in a flask which can be closed air-tight, and is treated with muriatic acid in the manner described at page 69. When the decomposition of the compound is fully effected, and every thing but the silicic acid is dissolved, liquid sulphuretted hydrogen is added to the solution. After some days, when the solution has become clear, the mixture of silicic acid and sulphur is separated by filtration, and washed. It is then permitted to become perfectly dry, and is afterwards cautiously treated with nitric acid, by which the sulphur is completely converted into sulphuric acid. The silicic acid is separated by filtration, and the sulphuric acid is precipitated from the liquid, by a solution of chloride of barium. It is necessary to treat the silicic acid a second time with fuming nitric acid, to ascertain whether it be altogether free from sulphur. From the weight of the sulphate of barytes, the quantity of precipitated sulphur is calculated, and this leads to the estimation of the quantity of peroxide of iron reduced by the liquid sulphuretted hydrogen to protoxide. The solution which has been filtered from the mixture of silicic acid and sulphur, is now to be mixed with nitric acid, for the purpose of oxidising the protoxide of iron it contains. The peroxide of iron is then to be precipitated, and weighed. The quantity of iron which it contains is calculated from its weight. The operator proceeds in the next place, to determine the quantity of the other constituents which have also been dissolved by the muriatic acid.

Another portion of the same substance is decomposed by muriatic acid, with the same precautions as the above, and also with the exclusion of atmospheric air. To the solution which is obtained, a solution of chloride of gold and sodium is added. After the lapse of some days, the solution is filtered from the insoluble remainder, which consists of a mixture of silicic acid and metallic gold. The mixture is washed, dried, ignited, and weighed. It is afterwards treated with aqua regia, which dissolves the gold, and leaves the silicic acid untouched. The quantity of gold which was mixed with the silicic acid, and has been dissolved, can either be determined from the loss of weight of the silicic acid, or by reprecipitation from the the solution. From the quantity of gold the quantity of protoxide of iron, contained in the substance submitted to analysis, is calculated.

XLIII. TANTALUM.

Quantitative Estimation of Tantalic Acid.—The native compounds of tantalic acid withstand the action of muriatic acid, and can only be decomposed by ignition with caustic or carbonated alcali. This operation produces tantalate of alcali. When the ignited mass is treated with water, this compound does not remain undissolved; but after the excess of alcali has been removed by water, the tantalate of alcali dissolves also. If the solution of the tantalate of alcali is saturated by muriatic acid, with a view to precipitate the tantalic acid, or if the ignited mass is treated directly with water and muriatic acid, it is very difficult, in either case, to obtain at once the whole of the tantalic acid. Besides the quantity which is thrown down at first, other portions have commonly to be separated from the other constituents of the mineral; the operation is consequently troublesome, and the result of the analysis uncertain. BERZELIUS (*Afhandlingar etc.* T. IV. p. 198) has therefore advised the decomposition of these compounds by fusion with bisulphate of potash, a process which yields much more satisfactory results than the above. To this end, the tantalate is pulverised and finely levigated with water. The powder is dried, and a weighed portion of it is mixed, in a large platinum crucible, with from six to eight times its weight of bisulphate of potash. The mixture is then heated by the flame of a spirit lamp with double current of air, till it becomes red hot and runs into fusion. As soon as the whole appears like a clear liquid, and no undissolved powder can be seen at the bottom of the crucible, it is permitted to cool. The melted mass is afterwards boiled repeatedly with a large quantity of water, until all the soluble matter has been extracted. The whole quantity of the tantalic acid, which had been dissolved by the fused bisulphate of potash, then remains undissolved, while the bases which were contained in the compound are dissolved in the free sulphuric acid of the bisulphate of potash. The solution containing the bases is filtered from the tantalic acid.

Separation of Tantalic Acid from the Oxides of Tin, Iron, Tungsten, and other Substances which occur with it in Tantalite.—Tantalic acid is separated in the above manner from nearly all the bodies with which it has hitherto been found combined. The tantalic acid, thus precipitated, is, however, according to BERZELIUS, not pure, but still combined with very small quantities of other substances, from which fusion with bisulphate of potash is incapable of separating it. These small quantities of foreign bodies consist principally of peroxide of tin, peroxide of iron, and often of tungstic acid, the whole of which must be quantitatively estimated. When, therefore, the undissolved tantalic acid has been properly edulcorated, it is next digested with bihydrosulphuret of ammonia. The effect of this is, to dissolve the tungstic acid and the peroxide of tin, and to convert the peroxide of iron into sulphuret of iron, which then remains undissolved with the tantalic acid, on which compound the bihydrosulphuret of ammonia has not the slightest action. The digestion is best performed as follows: The funnel upon which the impure nitric acid has been filtered is placed in a flask, and the neck of both is greased with tallow in such a manner, that the flask is closed quite air-tight by the funnel. Bihydrosulphuret of ammonia is then poured on the tantalic acid, and not being able to run down into the flask, remains a long time in contact with the tantalic acid. When the operator believes that the peroxide of tin and the tungstic acid have been completely converted into metallic sulphurets and dissolved, he allows the liquid to run down into the flask. The mixture of sulphuret of iron and tantalic acid still remaining in the filter is washed with water, to which a little bihydrosulphuret of ammonia has been added. When this has been done, and the funnel has been again fixed air-tight into the flask, muriatic acid is poured over the tantalic acid on the filter, and is allowed to digest therewith for a short time, in the same manner that the bihydrosulphuret of ammonia was previously permitted to do so. When the sulphuret of iron is dissolved, the solution is allowed to run down. The tantalic acid is then edulcorated with boiling water, dried, ignited, and weighed. For the sake of insuring the greatest degree of accuracy, it is proper, after having weighed the tantalic acid, to examine, by experiments with the blowpipe, whether it be free from peroxide of tin and tungstic acid.—BERZELIUS precipitates the solution in bihydrosulphuret of ammonia, by nitric acid, and treats the precipitate with aqua regia; the undissolved tungstic acid is then filtered, and is washed on the filter with water slightly acidulated. The peroxide of tin is precipitated from the solution in aqua regia by ammonia. The muriatic acid solution of iron is mixed with the liquid which was filtered from the impure tantalic acid. This mixed solution then contains iron with a portion of tin, the best separation of which is effected by sulphuretted hydrogen gas.

Separation of Tantalic Acid from Yttria, the Peroxide of Uranium, &c.—Analysis of Yttro-Tantalite.—The above is the method of analysis when the tantalic acid is combined with but small quantities of the bases, as is the case with the tantalites; but a different process is required, when larger quantities of the bases are present, as in the yttro-tantalites. The compound is, however, still fused with bisulphate of potash, and the fused mass treated with a sufficient quantity of boiling water. When this has been done, the solution is decanted, and the undissolved residue is digested for a considerable time with concentrated muriatic acid. The insoluble matter is then filtered and washed, and the muriatic acid solution is mixed with the other liquid. The insoluble matter is then digested with bihydrosulphuret of ammonia, and afterwards with muriatic acid, in the manner which has been described above. What remains undissolved, after this treatment, is tantalic acid.—The peroxide of tin and the tungstic acid are precipitated from the acid solution by sulphuretted hydrogen gas; and the resulting sulphurets are mixed with those which are precipitated by an acid from the solution in bihydrosulphuret of ammonia. To the solution filtered from the metallic sulphurets, a little nitric acid is added, and the whole is warmed; by this means, the protoxide of iron is converted into peroxide of iron, and, upon the addition of ammonia, a precipitate is formed which contains peroxide of iron, yttria, and peroxide of uranium; supposing the two latter to form part of the compound submitted to analysis. This precipitate is rapidly filtered, and the filtered solution is mixed with oxalate of ammonia in order to precipitate the lime. The precipitate of peroxide of iron, yttria, and peroxide of uranium, is redissolved in nitric acid. It frequently happens that, upon making this solution, a very small portion of tantalic acid remains undissolved, the quantity of which must be estimated. The precipitation of the peroxide of iron, from this solution, is effected by means of carbonate of ammonia. It is more difficult to separate the yttria and peroxide of uranium from one another.

Separation of Tantalic Acid from Silicic Acid.—Should tantalic acid have to be separated from silicic acid, the best method of operating would be, to treat the mixture, after ignition, with hydrofluoric acid, in a vessel of platinum. The silicic acid would then be dissolved, while the ignited tantalic acid would remain insoluble. According to BERZELIUS, however (POGGENDORFF'S Annalen, B. IV. p. 6), the tantalic acid takes up a little hydrofluoric acid, but loses it again on being exposed to ignition.

XLIV. CARBON.

Quantitative Estimation, by Combustion in the open Air.—The quantitative estimation of carbon can be effected by various methods; one or other of which is adopted according to the state in which the carbon exists in the substance to be analysed. When carbon is only mechanically mixed with other substances, or when it exists therein in an easily combustible state, then it is often merely necessary to ignite the substance in the open air, to effect its entire separation by combustion. The quantity of carbon is, by this method, determined from the loss of weight; but this method can only be followed in those cases, in which no other substance capable of being consumed or volatilized is present at the same time: when other volatile substances are present, the quantity of carbon cannot be estimated from the loss of weight occasioned by ignition. The plan has been put into practice, of analysing such substances by heating them in a small retort, with exclusion of atmospheric air, to separate the volatile constituents, of which the quantity is determined by the loss of weight. Thereafter, upon again igniting the substance, and this time with access of air, for the purpose of occasioning the combustion of the carbon, and upon again ascertaining the loss of weight, the operator finds the quantity of carbon. The results afforded by this method are, however, far from being accurate, and in many cases, do not even approach the truth; the cause of this is, that the volatile constituents very often form volatile compounds with the carbon.

Estimation by Conversion into Carbonic Acid.—To determine the quantity of carbon in a substance which, at the same time, contains volatile bodies, the common method of proceeding is, to convert the carbon, by oxidation, into carbonic acid, and then either to estimate the quantity of the carbonic acid from the bulk of the gas, or to lead it into lime water, or barytic water, to determine the weight of earthy carbonate produced, and thereupon to calculate the quantity of carbon. Different processes are followed, in the conversion of carbon into carbonic acid, according to the more or less intimate combination of the carbon with other substances, and according also to the particular nature of the combined substances.

Oxidation of Carbon, by Deutoxide of Copper.—The best method of oxidising the carbon, in a carbonaceous substance, is that which has been given by GAY-LUSSAC: A weighed portion of the compound is ignited in a proper apparatus with deutoxide of copper; the carbon reduces this oxide, becoming itself, when a sufficient excess of the metallic oxide is present, completely converted into carbonic acid. If the substance submitted to examination contain other constituents which can also reduce the deutoxide of copper, then the carbonic acid which is produced is commonly accompanied by other volatile substances. As it is almost always the case, that the carbon in carbonaceous bodies, which are to be decomposed by deutoxide of copper, is accompanied by hydrogen, on which account, the combustion with deutoxide of copper, produces both carbonic acid and water, so the circumstantial description of the apparatus necessary to be employed in this operation, and of the precautionary measures to be observed in conducting it, shall be given in the fifty-first section of this Part, which will treat at length of the means of effecting the quantitative estimation of hydrogen and of its compounds.

Oxidation of Carbon, by Oxygen Gas, Chlorate of Potash, and Nitrate of Potash.—Instead of deutoxide of copper, the analyst can, in many cases, employ oxygen gas, or chlorate of potash, and in some cases, nitrate of potash; the whole of which bodies are capable of converting carbon into carbonic acid. In the use of chlorate of potash, the operator, in most cases, employs an apparatus similar to that of which he makes use in the employment of deutoxide of copper. Nitrate of potash is, however, frequently employed, particularly when the substances to be quantitatively analysed are mixtures of carbon with other combustible substances which have been prepared for technical purposes. In this case, the operator generally estimates the quantity of the acids resulting from the oxidation of the other substances, which acids combine with the potash of the nitrate of potash: the whole quantity of the carbonic acid, or of the carbon, is then ascertained from the amount of the loss. It is possible, however, to determine also the quantity of the resulting carbonic acid; a portion thereof combines with the potash to carbonate of potash, while another portion is volatilized as carbonic acid gas.

Separation from other Substances by Muriatic Acid.—When carbon is combined with substances which are soluble in non-oxidising acids, such as muriatic acid, then, by treating such substances by these acids, the carbon is obtained as an insoluble remainder: the operator gathers it upon a weighed filter, washes and dries it; and when it is perfectly dry, determines its weight. It is difficult, however, to weigh pulverulent charcoal with great accuracy when it is present in large quantities; but it can be done with small quantities. The operator must never neglect, after weighing, to burn the charcoal in the open air, in order to see whether it contain any foreign matters; the ashes which may be left are weighed and deducted from the weight of the charcoal.—When, however, the substances combined with the carbon dissolve in diluted muriatic acid, under decomposition of water and disengagement of hydrogen gas, then is the present method impracticable, because the disengaged hydrogen forms volatile compounds with carbon, which fly off in the state of gas.

Separation from Siliceous Substances.—Carbon occurs but seldom in siliceous substances. BERZELIUS, in the analysis of the Pyorthite (*Afhandlingar*, T. v. p. 52), the only native silicate containing a considerable quantity of carbon which has hitherto been examined, determined the quantity of carbon from the loss which a weighed portion of the mineral suffered on being ignited in the open air. But as, in this compound, not only carbon, but water is contained, it is necessary to submit another weighed portion of the mineral to ignition, in a retort, with exclusion of atmospheric air; the loss which is then suffered, gives the quantity of water and of other volatile parts.

Separation from Phosphorus.—Carbon produces with phosphorus no compounds which have been accurately examined. When phosphorus contains carbon, the two substances can be separated by heating the compound to redness, with exclusion of atmospheric air.

Separation from Sulphur.—The compound of sulphur and carbon was examined by BERZELIUS and MARCET (SCHWEIGGER'S *Jahrbuch*, T. IX. p. 293) in the following manner: The vapour of sulphuret of carbon was led over peroxide of iron which had been previously brought to a red heat. The products were sulphuret of iron and carbonic acid gas, the latter of which was collected over mercury. At the same time, however, a small quantity of sulphurous acid was also produced; this was obtained in the gaseous state, in company with the carbonic acid gas. The peroxide of iron was placed in a glass tube, which was kept in a state of ignition during the operation. The vapour of the sulphuret of carbon was led over it exceedingly slowly and uniformly. This was brought to pass as follows: The sulphuret of carbon was placed in a small retort, and weighed in it. The retort was then connected, air-tight, with that part of the glass tube which was not ignited. To vaporize the sulphuret of carbon, the retort was heated by a lamp which was placed only *near* and not *below* it. The flame of the lamp produced a sufficient degree of heat, by radiation, to make the gas produced by the decomposition pass into the glass receiver standing over the mercury, at the rate of about one bubble of gas in every minute. The radiating heat of the furnace in which the glass tube with the peroxide of iron was ignited, was prevented from having any effect on the retort, by the interposition of a sheet of plate iron.—At the end of this operation, the peroxide of iron, which was for the most part converted into sulphuret of iron, was carefully treated with aqua regia, and the quantities both of the resulting sulphuric acid, and of the precipitated sulphur, were carefully determined.—Then, in order to separate the gases which had been received in the glass over the mercury, the following process was adopted: A small glass was filled with a weighed quantity of brown oxide of lead; it was then covered with glove-leather, fastened to an ignited fine iron wire, and introduced into the receiver through the mercury. The sulphurous acid became oxidised by the brown oxide of lead, and produced sulphate of protoxide of lead. After the lapse of twelve hours, a second glass, filled with caustic potash, was introduced into the receiver in the same manner. The object of this was, to absorb the carbonic acid gas. When the absorption appeared to be at an end, and the receiver seemed to contain nothing but the atmospheric air, with which, previous to the experiment, the apparatus was filled, then the little glasses were weighed; the increase of weight gave the quantity of sulphurous acid, and of carbonic acid produced. Thus, from these data, the composition of the sulphuret of carbon, could be readily determined.

When, on the contrary, it is merely a mechanical mixture of sulphur and charcoal which is to be quantitatively estimated, then the best mode of proceeding is to expose a weighed quantity of the substance to a slow heat, with the exclusion of atmospheric air: the sulphur thereupon volatilizes, while the charcoal remains behind, and can be weighed. In order completely to hinder the access of atmospheric air, the mixture is heated in a gas, by which charcoal is incapable of being affected. The gas which it is most advisable to employ in this case is hydrogen gas. The operation is performed in an apparatus such as that described at page 83. The mixture is placed in the glass bulb *g*, which is then weighed. The sulphur which is separated by sublimation is driven by the flame of a small spirit lamp completely out of the glass tube. When the whole is cold, the glass bulb *g* is again weighed, upon which the quantity of charcoal is at once ascertained.

If the operator, instead of determining the quantity of sulphur from the loss, wishes to determine it by a direct experiment, he must oxidise the sulphur to sulphuric acid, and precipitate the sulphuric acid by the solution of a salt of barytes. The oxidation of the sulphur, in a mixture of charcoal and sulphur, is most easily effected, according to GAY-LUSSAC (*Annales de Chimie,* T. XVI. p. 435), by the following process: A weighed quantity of the mixture is accurately mixed, first with carbonate of potash, and then with nitrate of potash and chloride of sodium; the mixture is afterwards exposed to the fire. A platinum crucible can be employed for this purpose, as the mixture does not attack the platinum. The mixture burns very quietly, and at last becomes white. When the remainder is cold, it is dissolved in water; the solution is cautiously acidulated by muriatic acid, and is then precipitated by a solution of chloride of barium. From the weight of the resulting sulphate of barytes, the quantity of sulphur is reckoned.—The addition of carbonate of potash is necessary, to prevent the volatilization of any sulphur: the chloride of sodium is added to modify the violence of the combustion. The proportions of the mixture are,—for one part of the mixture of charcoal and sulphur, 4 parts of carbonate of potash, 7 or 8 parts of nitrate of potash, and 16 parts of chloride of sodium.

Separation from Sulphur and Saltpetre: Analysis of Gunpowder.—It is very easy to determine, in this manner, the quantitative composition of gunpowder. To determine the quantity of the saltpetre, a weighed quantity of the gunpowder is treated with water; the solution, filtered from the insoluble mixture of charcoal and sulphur, is then evaporated to dryness. To determine the quantity of the charcoal, the mixture of charcoal and sulphur, separated by filtration from the solution of saltpetre, is first carefully dried, and weighed upon a weighed filter. Thereupon, an accurately-determined portion of it is taken from the mass, and is treated in the manner described above, for determining the quantity of charcoal. To determine the quantity of the sulphur, another portion of the gunpowder is mixed with an equal quantity of carbonate of potash, with an equal quantity of saltpetre, and with four times as much common salt. The mixture is then treated in the manner described above.

Separation from Iron by Muriatic Acid.—The examination of the compounds of carbon with metals, is often accompanied by the greatest difficulties. We are acquainted with but very few of such compounds; the most important of these are unquestionably the compounds of carbon with iron, the knowledge of which can often be of great consequence in a technical point of view. By treating carbonaceous iron with diluted non-oxidising acids, such, for example, as muriatic acid, a smaller quantity of hydrogen gas is produced than would be produced by treating an equal weight of pure iron by those acids. In the former case, a portion of the carbon combines with hydrogen, and produces a volatile oil; after the solution of the iron, the insoluble residue presents nothing near like the whole quantity of carbon. The quantity of carbon could, it is true, be estimated from the loss, if the quantity of iron were first estimated. To do this, the solution of the carbonaceous iron in muriatic acid, must be treated with nitric acid, to convert the protoxide of iron into peroxide of iron; and from the quantity of peroxide of iron obtained by precipitation, the quantity of iron must be calculated. If, in this case, the solution of the peroxide of iron, or the substance left undissolved by the acid, should contain small quantities of protoxide of manganese, magnesia, sulphuric acid, phosphoric acid, or silicic acid, then, these substances can be quantitatively estimated, according to the methods given in the preceding pages, either by precipitating them from the solution of peroxide of iron, or by analysing the insoluble residue, after having ignited it in the open air to get rid of the charcoal. These substances are contained in the carbonaceous iron, in the state of manganese, magnesium, sulphur, phosphorus, and silicium.

Separation from Iron by Chloride of Silver.—As, however, the quantity of carbon in iron is commonly very small, its quantitative estimation by the above process, is in the highest degree uncertain. In consequence of this uncertainty, various methods have been recommended, of determining the quantity of charcoal by direct experiments. The most unobjectionable is that of **Berzelius** (*Lehrbuch*, Uebersetzung von **Wöhler**, T. II. p. 383), which is performed as follows: The operator fuses chloride of silver to a cake, and places the cake in a vessel with water; the vessel being of such a description that it can be closed by a glass plate, so that its contents may be protected from the action of atmospheric air. The operator then places the piece of carbonaceous iron which is to be analysed, upon the cake of chloride of silver. The chloride of silver is reduced by the iron, which becomes converted into protochloride of iron, and is dissolved by the water. The charcoal remains undissolved upon the partly-reduced chloride of silver: it can be easily separated, and gathered upon a weighed filter. This operation lasts a long time, when the piece of iron is massive. The chloride of silver must be used in excess; more than 5½ parts of it must be employed to 1 part of iron.

Separation from Iron, by Chlorine Gas.—According to another method, also described by **Berzelius**, a weighed quantity of the carbonaceous iron, is treated in an apparatus similar to that represented at page 83, with a current of dry chlorine gas. The iron is brought to ignition, and the operator endeavours to expel the resulting perchloride of iron from the glass bulb, by sublimation; the charcoal remains behind, and can be weighed.—In this operation, care must be taken that the gaseous chlorine which passes over the ignited iron, be not accompanied by oxygen gas or atmospheric air; otherwise, a portion of the carbon can easily be volatilized in the state of gaseous carbonic oxide or carbonic acid. It being often difficult to prevent this, one might probably with greater advantage, make use of bromine in this experiment. In that case, a weighed quantity of the carbonaceous iron to be examined, should be placed in a vessel, have water poured over it, and bromine added; thereupon, perbromide of iron would be produced, and dissolved in the water, and the charcoal would remain behind. The solution should be filtered through a weighed filter, upon which filter the charcoal should be dried and weighed.

Separation from Iron, by Oxygen Gas.—A third method recommended by BERZELIUS, consists in heating the carbonaceous iron to redness, while a current of dry oxygen gas is slowly passed over it. The iron is converted into the intermediate oxide of iron, and the carbon into carbonic acid gas. That the carbonic acid may be collected without loss, all the gas which issues from the apparatus is carefully passed into lime water or barytic water, as long as it produces a precipitate. From the weight of the resulting earthy carbonate, the quantity of carbon is calculated.

Analysis of Cast Iron: a. *Estimation of the Carbon.*—In the quantitative estimation of the carbon contained in iron, one thing which should always be taken into consideration is the state in which the carbon exists in the iron. According to KARSTEN, the grey sort of cast iron not only contains a portion of carbon chemically combined with the iron, and constituting carburet of iron, but also another portion of carbon combined merely mechanically with the iron, in the state of pure crystalline carbon, or Graphite. It was formerly thought, that Graphite was a chemical compound of a small quantity of iron with a large quantity of carbon; but it has at length been demonstrated by KARSTEN, that it consists of pure carbon alone. To determine the quantity of iron existing in a specimen of cast iron, KARSTEN (*Handbuch der Eisenhüttenkunde,* T. I. p. 370), proceeds as follows: A weighed quantity of the cast iron is dissolved in nitric acid to which a little muriatic acid has been added. The residue contains the crystalline carbon, or graphite, together with a compound of carbon, which resembles extractive matter and proceeds from the carbon of the carburet of iron. It also contains silicic acid, and the oxides of some metals which were combined with the iron. The residue is treated with a solution of caustic potash, by which the silicic acid, if any is present, and the carburet which resembles extractive matter, are dissolved; while the graphite, on the contrary, remains unattacked. After being washed, the residue may still be treated by muriatic acid, that all impurities may be effectually removed. It is then washed, dried, and weighed.—If now the operator has determined the whole quantity of the carbon contained in the iron, by means of an experiment with chloride of silver, it only remains to deduct therefrom the weight of the Graphite, to learn the quantity of the carbon which was chemically combined with the iron, to carburet of iron. It is, however, necessary to take into consideration, that the carbon separated by chloride of silver may contain both silicic acid and various other substances, all of which must be quantitatively estimated and deducted from the weight of the carbon.

As the carbonaceous irons contain the other constituents in still smaller quantity than the carbon, and as it may often be of importance to know the quantity of each with accuracy, it is proper to undertake a separate analysis for the determination of each of these constituents.

— b. *Estimation of the Sulphur.*—The quantity of sulphur contained in iron is, according to KARSTEN (*Handbuch der Eisenhüttenkunde,* T. I. p. 408), so inconsiderable, even in *hot short iron,* that, after oxidising the compound by aqua regia, the precipitation of the resulting sulphuric acid by a solution of barytes affords results which are by no means satisfactory. To determine the quantity of sulphur, therefore, it is better to dissolve the iron in muriatic acid, and to separate the whole of the sulphur, in the state of sulphuretted hydrogen gas. For this examination, about 80 grains of iron should be employed. It must be broken into pieces of the size of millet seeds. The apparatus necessary to be employed in this experiment, is the same as that represented at page 229. No heat is to be applied to facilitate the solution. The flasks must contain a metallic solution, and one of perchloride of copper answers the purpose best. The decomposition of the sulphuretted hydrogen gas, provided it be very slowly disengaged by the iron, is completely effected by the solution in the first flask; it is therefore unnecessary to place more than two flasks in connection with the apparatus. For perfect solution, the various sorts of crude iron require from ten to fourteen days, of steel from eight to ten days, and of bar-iron from three to four days. To drive the sulphuretted hydrogen gas, which, after the complete dissolution of the iron, may remain in the flask *a*, completely out of that flask and into the solution of chloride of copper, it is necessary to employ carbonic acid gas, which must be applied in the manner described at page 230.

— c. *Estimation of the Phosphorus.*—To determine the quantity of phosphorus contained in the carbonaceous iron, another portion must be dissolved in nitric acid, with the aid of heat; the phosphorus is thereby converted into phosphoric acid. Instead of nitric acid, the operator can employ aqua regia to dissolve the iron; but nitric acid is best. Between 40 and 50 grains is a sufficient quantity of iron to be employed in this experiment. The solution is evaporated to dryness in a porcelain capsule, and is heated as strongly as possible in the same vessel. The dry mass is then mixed, in a platinum crucible, with three or four times its weight of carbonate of potash, and is therewith ignited. The ignited mass, after cooling, is treated with water, in which the phosphate of potash and the excess of carbonate of potash dissolve, while the peroxide of iron remains undissolved, and can be separated by filtration. If the iron submitted to analysis contained sulphur, then the solution, filtered from the peroxide of iron, contains sulphate of potash; and if the iron contained manganese, the solution contains manganesiate of potash. When, however, the solution is boiled for a long time, the manganesiate of potash is decomposed, and brown flocks of peroxide of manganese are deposited. The filtered solution is cautiously supersaturated with nitric acid, and, if silicium was combined with the iron, is evaporated to dryness, to separate the silicic acid. The dry mass is moistened with nitric acid, and after some time is treated with water, upon which the silicic acid remains undissolved. The filtered solution is mixed with ammonia, which, if aluminum was combined with the iron, produces a precipitate of basic phosphate of alumina. The alcaline solution is then very weakly acidulated by acetic acid, and the phosphoric acid is precipitated by a solution of acetate of lead. The precipitated phosphate of lead is treated in the manner which has been described at p. 263. The operator must bear in mind here, that if the iron submitted to analysis contained sulphur, the phosphate of lead can be accompanied by sulphate of lead. But since the quantity of sulphur has been determined by a different experiment, it is easy to calculate how much sulphate of lead is capable of being thus produced. The quantity of the protoxide of lead being then determined, it is found at once, how much was combined with sulphuric acid, and how much with phosphoric acid.—This method of estimating the small quantity of phosphorus contained in iron, or rather of phosphoric acid contained in the nitric acid solution, is preferable to that, in which the solution is supersaturated with ammonia, and the phosphoric acid separated by bihydrosulphuret of ammonia. By the latter method, a very small quantity of phosphoric acid, can be very easily overlooked, if the whole has not been digested together for a sufficient length of time.

— d. *Estimation of the Chromium.*—Should chromium be contained in the carbonaceous iron submitted to examination, the quantity of it can be determined in the same manner as the quantity of phosphorus. By ignition with carbonate of potash, chromate of potash is produced, and this, with the phosphate of potash, dissolves in water. The subsequent treatment is the same as in the preceding case. A precipitate is thrown down by the solution of lead, which contains chromate of lead, and if phosphorus be present, phosphate of lead, which is coloured yellow by the chromate of lead. After the precipitate is weighed, it is treated with muriatic acid and alcohol, upon which phosphate of lead and chloride of lead remain undissolved, while the oxide of chromium resulting from the decomposition of the chromate of lead is dissolved by the acid. The solution is filtered, the alcohol is expelled by heat, and the oxide of chromium is precipitated by ammonia.

— e. *Estimation of the Silicium.*—The silicium contained in iron must be sought for as silicic acid, partly in the residue left by the solution, partly in the acid solution itself.

— f. *Estimation of the Titanium.*—The estimation of titanium, which, when it occurs with iron, can only be present in extremely small quantity, since titanium does not appear to form an alloy with iron, can only be effected by one method of proceeding, that, namely, in which the nitric acid solution is treated in the manner described at page 170.

— g. *Estimation of the Manganese.*—To determine the proportion of manganese contained in iron, it is necessary to treat the solution of iron in the manner which has been described at page 55. In consequence of the very large proportion of peroxide of iron in the solution, in the present case, it is by no means difficult to estimate even a very small proportion of manganese with much accuracy.

Quantitative Estimation of Carbonic Oxide Gas.—Of the oxides of carbon, the operator has seldom to estimate carbonic oxide gas. The quantitative analysis of this compound is effected by converting it, by detonation with oxygen gas, into carbonic acid gas: the quantity of the carbonic oxide gas in then calculated from the bulk or the weight of the carbonic acid gas. A sufficient quantity of the carbonic oxide gas to be examined, is passed into a graduated tube, standing over mercury, and furnished with wires to conduct the elective spark; the volume of the gas is then accurately determined; after which, rather more than half as much oxygen gas is added, and the electric spark is passed through the gaseous mixture. When the carbonic oxide gas is very pure, then a volume of carbonic oxide gas gives a volume of carbonic acid gas. When therefore a volume of carbonic oxide gas has been mixed with precisely half a volume of oxygen gas, the mixture of gases is reduced in bulk, by the detonation, to one volume. But, now, in order to learn with still greater accuracy the quantity of the resulting carbonic acid gas, the operator, after having first determined the volume of the gas after detonation, proceeds to separate the carbonic acid gas. For this purpose, he fastens a small stick of caustic potash, which must previously have been very slightly moistened, upon a fine iron wire, commonly employing fine ignited harpsichord wire, and then passes it through the mercury into the gas. The carbonic acid gas is absorbed by the potash; in proportion as the mercury rises in the tube, in consequence of this absorption, the wire with the potash is also pushed higher in the tube, so that the potash always appears above the surface of the mercury. When absorption no longer takes place, the potash is drawn out of the tube by the wire, and the volume of the remaining gases is accurately determined. In this manner the volume of the carbonic acid gas is determined with accuracy, upon which the operator can easily determine the quantity of the carbonic oxide gas. The gas which remains, when the carbonic oxide gas has been pure, is oxygen, which must be always added in excess. With respect to the precautionary measures, which are necessary to be followed in this experiment, they are the same as those which are to be followed in the quantitative estimation of gases in general. These precautionary measures will be circumstantially described in the 51st section, in which the analysis of most gases will be taken into consideration.

Quantitative Estimation of Oxalic Acid.—The quantitative estimation of the second oxide of carbon, or oxalic acid, is best effected by precipitating it from its solutions, by a solution of lime, in the state of oxalate of lime. When, therefore, the oxalic acid is dissolved in a liquid, it is saturated as accurately as possible with ammonia, and the solution is diluted with water. The operator then adds a solution of a neutral calcareous salt, generally a solution of chloride of calcium, which is that which, in most cases, is best adapted to the purpose. The resulting oxalate of lime is washed. The quantity of the oxalic acid could very well be calculated from the weight of the oxalate of lime; but as it is very difficult perfectly to expel the water from the oxalate of lime by drying, and as it is very unsafe to estimate that salt in the hydrous state, so it is best to convert the oxalate of lime, by ignition, into carbonate of lime, and to calculate the quantity of the oxalic acid from the weight of the carbonate of lime. The conversion of oxalate of lime into carbonate of lime is effected by the process described at page 17.—Care must be taken, in the precipitation of oxalate of lime, that the solution contain no free ammonia; because then, the access of atmospheric air would cause, after some time, the precipitation of carbonate of lime in company with the oxalate of lime.

Estimation of the Oxalic Acid in Soluble Oxalates.—The estimation of the oxalic acid in the oxalates which are soluble in water, is effected in the same manner as the estimation of free oxalic acid. If the operator have a neutral oxalate to examine, it is merely dissolved in water and precipitated by a solution of a neutral salt of lime. But if the oxalate which is to be examined, be acid, then the solution must previously be accurately saturated with ammonia.—As the neutral oxalates of potash and soda are converted by ignition into neutral carbonates of those alcalies, it is very easy to ascertain the quantity of oxalic acid they contain: it is only necessary to expose a weighed quantity of the oxalate to ignition, and to determine the weight of the resulting carbonate; after which, the quantity both of the oxalic acid and of the water of crystallisation, can be easily reckoned.

Estimation of the Oxalic Acid, in insoluble Oxalates.—In the oxalates which are insoluble in water, the oxalic acid must be determined otherwise. If they contain no water, a weighed portion may be ignited with access of air; in most cases, the base alone then remains behind, and can be weighed. The loss of weight gives the quantity of oxalic acid. Many metallic oxalates are completely reduced by being ignited in closed vessels, where atmospheric air has no access.—When, however, the insoluble oxalate contains water, and the operator is nevertheless desirous of determining the quantity of oxalic acid by a direct experiment, then, the oxalate can, in most cases, be decomposed, by being boiled a sufficient time with a solution of carbonate of potash. If the compound formed by the base of the oxalate with the carbonic acid, be insoluble, it remains undissolved, while the oxalic acid combines with the potash and dissolves. The solution after filtration, is accurately saturated with muriatic acid, and the oxalic acid is precipitated by a neutral solution of lime.

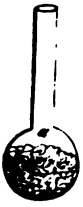
Estimation of the Carbonic Acid, in the gaseous state.—The quantitative estimation of the third oxide of carbon, or carbonic acid, has very frequently to be effected. There are various methods of proceeding. If the carbonic acid of which the quantity is to be estimated, be in the gaseous state, then it is best, first accurately to measure the volume of the gas, in a graduated glass tube, standing over mercury, and then to introduce through the mercury into the tube a small stick of caustic potash, which has previously been slightly moistened and fastened to an ignited harpsichord wire. The carbonic acid is absorbed by the potash. When absorption ceases, the wire with the potash is drawn from the tube, and the volume of the unabsorbed gas is accurately determined: the difference in the two measurements of the volume of gas, shows the quantity of the carbonic acid.

When, on the contrary, the carbonic acid gas is contained in a large and not graduated glass receiver, standing over mercury, the operator places a portion of caustic potash in a small glass, covers it with glove leather, and, when it has been accurately weighed and fastened to an ignited harpsichord wire, passes it through the mercury into the receiver. The carbonic acid is slowly absorbed; when, after some time, the absorption has ceased, the operator draws the small glass by the wire from the receiver, cleanses it from the drops of mercury which hang about it, and ascertains the weight. The increase of weight of the potash shows the quantity of absorbed carbonic acid.—It will be understood, that this method of estimating carbonic acid gas, cannot be employed when that gas is mingled with other gases which can also be absorbed by caustic potash.

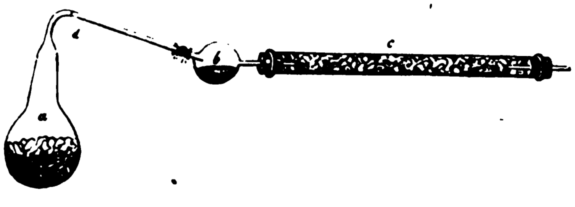
Separation of Carbonic Acid from solid Carbonates, by Ignition.—When the carbonic acid is contained in solid substances, its quantitative determination is effected by different processes, according as it can be separated from the bases by ignition, with ease or with difficulty. Most of the compounds of carbonic acid are of such a nature, that, when ignited over a spirit lamp with circular wick, they completely lose their carbonic acid. The quantity of carbonic acid contained in such compounds can therefore be very accurately estimated from the loss of weight occasioned by ignition, provided the carbonic acid be not accompanied by other volatile constituents. In the compounds formed by carbonic acid with all the metallic oxides, properly so called, as also in that formed with magnesia, the quantity of carbonic acid can, in this manner, be properly estimated; after the ignition, the metallic oxide, or the magnesia, remains behind in a state of purity. When the metallic oxide is one of those which are very easily reducible, as, for example, protoxide of lead, oxide of cadmium, &c., the ignition must be performed in a small weighed porcelain crucible; when this is not the case, a platinum crucible can be employed.

Separation of Carbonic Acid from the Oxides of Iron, Manganese, and Cobalt.—There are some carbonates which can, indeed, be easily deprived of their carbonic acid by ignition, but which contain metallic oxides that are capable of being more highly oxidised by the action of the air during ignition; such, for example, are the carbonates of protoxide of iron, of protoxide of manganese, and of oxide of cobalt: with these carbonates a different method of analysis must be adopted. They can be ignited in an atmosphere of some gas, in which the metallic oxides are incapable of becoming more highly oxidised. Of all the gases which can be easily procured, none but nitrogen gas and carbonic acid gas are adapted to this purpose; for all other gases act upon the ignited metallic oxides, either in such a manner as to reduce them or to produce some new compound. As it would be difficult to conduct a current of nitrogen gas over the weighed compound, while in a state of ignition, the analyst commonly employs a current of carbonic acid gas for this purpose; although it is more difficult to expel carbonic acid from a carbonate, by ignition in an atmosphere of carbonic acid gas, than by ignition in an atmosphere of any other kind of gas. The apparatus employed in this experiment is such as that described at page 83. The compound for examination is weighed in the glass bulb g, which is then connected with the flask in which the gas is to be produced. The current of carbonic acid gas is best produced by employing chalk and diluted nitric acid, or, what is preferable, diluted sulphuric acid. That the gas may be dried, it is passed through a tube containing chloride of calcium. When the whole apparatus is full of carbonic acid gas, the operator gradually applies heat to the bulb, by means of a spirit lamp with circular wick; the bulb must be heated to redness, and a red heat kept up pretty long. The carbonic acid gas is allowed to pass over the compound during the whole time of cooling; when it is cold, the glass bulb with the oxide is weighed. The loss of weight, occasioned by the ignition, indicates the quantity of carbonic acid contained in the compound submitted to analysis. It is necessary, after weighing the glass bulb, to connect it again with the apparatus and to ignite it afresh, in order to ascertain whether the whole of the carbonic acid be expelled, or a second loss of weight be produced. The ignited compound must finally be subjected to the action of water and muriatic acid, in order to prove, by that test, whether any carbonic acid remain present. WALMSTEDT (SCHWEIGGER'S *Jahrb.* XXXV. p. 400) was the first who employed this method.—The operator proceeds in the same manner, when the above-named oxides are accompanied by other bases in combination with carbonic acid; this is what is most frequently found to be the case, for these oxides seldom occur singly, in combination with carbonic acid. When, however, carbonate of lime forms a constituent of the compound to be examined, this method cannot be made use of, because ignition produced by the flame of a spirit lamp with circular wick, is by no means sufficient to expel the carbonic acid from the carbonate of lime; the heat, indeed, effects a partial decomposition of the calcareous salt, but the discharge of the carbonic acid is far from being complete.

Estimation of the Quantity of Water contained in Hydrous Carbonates.—When a carbonate which can be easily deprived of its carbonic acid by ignition, contains water, the quantity of the water must necessarily be determined, as well as that of the carbonic acid. To this end, the carbonate must be ignited in a little retort, which must have been weighed first empty, and then with the portion of compound for examination; the disengaged water must be collected and weighed. Upon deducting the weight of the water collected, from the whole loss of weight sustained by the carbonate submitted to ignition, the result gives the quantity of carbonic acid contained in the compound. The best method of proceeding, in this experiment, is as follows:



The operator first blows a glass bulb at the end of a glass tube, which must be of strong glass, so as to form a small matrass, as represented in the annexed figure. When he has determined the weight of this matrass, he places therein such a quantity of the carbonate as he may have determined to submit to analysis. He then weighs the whole, and thus ascertains the weight of the portion of the compound employed in the experiment which is to follow. The tube of the glass matrass, at about half an inch from the bulb, is now drawn out to a point, and, at the same time, is bent in such a form as to represent a small retort, which is exhibited by the figure *a*, below. This is again weighed, and is then connected, by a tube of Indian rubber, with the small receiver, *b*. The point of the receiver *b* passes into a small glass tube, *c*, which is filled with chloride of calcium. The receiver *b*, the tube *c*, and the Indian rubber tubes, are weighed before the experiment. When the apparatus is set together, the bulb *a* is thoroughly heated, for a long time, with the spirit lamp. The greater part of the separated water collects in the receiver *b*; a



smaller portion is carried farther in the state of vapour, but is completely absorbed by the chloride of calcium in the tube *c*. If the glass bulb, *a*, be of very strong glass, such a degree of heat may be applied as is sufficient completely to expel the carbonic acid. After cooling, the neck of the retort is cut off at *d*, because a drop of water remains hanging at the point; the receiver *b*, with the tube *c*, and the neck of the retort, are weighed together. The weighing, however, is not effected immediately; the operator waits until the heavy carbonic acid has been expelled from the apparatus by the air of the atmosphere. The neck of the retort is then dried and weighed by itself. The increase of weight received by the receiver *b* and the tube *c*, deducting the weight of the dried point of the retort, indicates the quantity of water. The operator now weighs the retort *a*, and adds the weight of the neck. From the loss of weight sustained by the retort, the common weight of the water and carbonic acid is ascertained. But as, now, the separate weight of the water is known, it is easy to find the quantity of the disengaged carbonic acid.

As the hydrous carbonates completely lose their water on the application of a moderate heat, with much more readiness than their carbonic acid, which is often not wholly expelled even by the application of a very strong heat, the best method of proceeding is to estimate, in the manner just described, the weight of the water alone, and then to determine the common weight of the water and the carbonic acid, by igniting another weighed portion of the compound in a platinum crucible. The quantity of the carbonic acid alone, can also be estimated by a direct experiment, the method of performing which will be described presently.

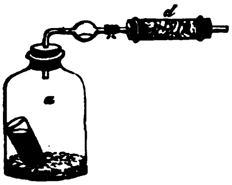
Separation of Carbonic Acid from Alcalies and Alcaline Earths, by stronger Acids.—From the compounds which carbonic acid forms with fixed alcalies, as well as with barytes, strontian, and even with lime, the carbonic acid cannot be expelled by ignition. Lime is included in this list, because the carbonate of lime, when ignited in a platinum crucible over the spirit lamp with circular wick, does not lose the whole of its carbonic acid. To determine the quantity of carbonic acid contained in these compounds, the operator has therefore to employ other processes, which processes, however, are capable of being employed with all other carbonates.

The quantity of carbonic acid contained in a compound, can be found by determining the volume of the carbonic acid gas expelled, from a weighed quantity of the compound, by means of a stronger acid. To this end, the operator passes a little muriatic acid into a graduated glass tube, filled with and inverted over mercury; he then allows a small weighed portion of the carbonate to rise through the mercury into the tube; the carbonic acid is thereupon expelled by the muriatic acid. When the volume of the carbonic acid gas ceases to increase, the surface of the mercury in the glass tube is brought on a level with the surface of the mercury on the outside of the glass tube; the volume of the gas is then measured.

This method is, however, not much to be recommended, as it is capable of giving incorrect results. The operator cannot with certainty know how much carbonic acid gas is absorbed by the liquid muriatic acid; and it is, besides, necessary to operate with quantities of carbonates so small, that uncertainty in the results is in part the consequence of the diminutiveness of the materials. It is better, therefore, to employ larger quantities of the carbonates, and to determine the quantity of carbonic acid they contain by another method. A weighed quantity of a carbonate may be decomposed by a weighed quantity of an acid; and after complete decomposition, the quantity of the discharged carbonic acid may be estimated from the total loss of weight.

To put this method of quantitatively estimating carbonic acid into practice, it is only necessary to proceed as follows: A sufficient quantity of the acid which is to be employed in the decomposition of the carbonate, is weighed, in a convenient glass, by means of a balance which, when pretty heavily laden, is still sensible to a small increase of weight. A weighed quantity of the carbonate is then added to the weighed acid. When the operator has taken care that no portion of the acid or carbonate has been thrown out of the glass by the effervescence, the way to hinder which is to place a concave glass over the vessel wherein the decomposition is effected, then, after the complete decomposition of the carbonate, the difference in weight indicates the quantity of the expelled carbonic acid.

Still, even this is no method which can give a very accurate result. As the operation often continues a very long time, before the decomposition is completely effected, it is easy for a portion of the acid employed in effecting the decomposition, to volatilize; or, supposing the acid to be difficultly volatilizable, but to be in a diluted state, then, a portion of the water may be vaporised. A still greater loss is experienced when the operator is obliged to apply a gentle heat to bring the decomposition to a conclusion, a case which often presents itself. In order entirely to prevent this loss, the experiment may be performed as follows:



The operator places in the flask *a*, which has a pretty wide mouth, but one that can be closed by a cork, a weighed quantity of the carbonate which is to be analysed, and then introduces, through the mouth of the flask, the little vessel *b*, containing a quantity of muriatic, or some other acid, sufficient to effect the decomposition of the carbonate. The acid and the carbonate are not allowed to come into contact. The little vessel, *b*, should be a bit of barometer tube of wide diameter and closed at the end; when filled with acid, and introduced into the vessel *a*, the top of the former should lean against the side of the latter. The flask is closed with a cork, through which a tube for conducting gas passes; the gas-conducting tube is connected by a tube of Indian rubber, with a little glass tube, *d*, filled with chloride of calcium. The whole is now weighed on a balance which, when pretty heavily laden, is still sensible to the action of very small weights; or rather, instead of being weighed, it is counterpoised. When this is done, the flask *a* is shaken so as to overturn the little vessel, *b*, which contains the acid. The acid then comes into contact with the carbonate, and effects the desired decomposition. All the water which, in performing the experiment with different apparatus, could be lost by effervescence or vaporisation, is, in the present case, absorbed by the chloride of calcium in the tube *d*. If the carbonate be difficultly decomposable, and it is necessary to apply heat, the operator can warm the flask *a*, without having any occasion to fear loss by evaporation. When the decomposition is fully accomplished, the cork is removed for a short time, that the carbonic acid gas remaining in the flask *a*, may mingle with atmospheric air, and be thus expelled from the flask. The operator then closes the flask, and determines its weight, yet not till the next day. The loss of weight indicates the quantity of carbonic acid discharged.

With respect to the decomposition of carbonates by acids, it is to be remarked that some of them are decomposed with great ease, and others not without much difficulty. There are some which are easily and fully decomposed, only when first reduced to powder, and then acted upon by acids, not in too concentrated, but rather in a somewhat diluted state.

XLV. BORON.

Quantitative Estimation of Boracic Acid.—The quantitative estimation of boracic acid is accompanied by many difficulties. When it is contained in a solution, and no other acid, or only nitric acid, accompanies it, it is possible to estimate it in the same manner that arsenic acid and phosphoric acid are estimated; namely, by adding to the solution an accurately-weighed quantity of pure and recently-ignited protoxide of lead, thereupon evaporating the solution to dryness, and igniting the residue in a small counterpoised platinum capsule. The quantity of the boracic acid is then found by deducting the weight of the protoxide of lead from that of the ignited mass.—It is impossible to effect the estimation of boracic acid by evaporating its solution to dryness, because a portion of the boracic acid is volatilized with the vapour of the water or alcohol in which the acid is dissolved.

There is no method of effecting the direct estimation of boracic acid, by throwing it down as an insoluble precipitate, and calculating the quantity of the acid from the weight of the precipitate; for, boracic acid produces with no base, a compound that is perfectly insoluble in water. The most accurate method of finding the quantity of boracic acid in the borates, consists in determining the quantity of the bases or substances combined with the boracic acid, existing in a weighed quantity of the borates, and then calculating the quantity of the boracic acid from the loss of weight.

Separation of Boracic Acid from Metallic Oxides.—The separation of boracic acid from the metallic oxides which are precipitable from acid solutions by sulphuretted hydrogen gas, or from neutral solutions by bihydrosulphuret of ammonia, is effected in the same manner as the separation of phosphoric acid from those metallic oxides. The method of operating is described at pages 251 and 253.

Separation of Boracic Acid from Lime, Strontian, Barytes, and Protoxide of Lead.—Barytes is separated from boracic acid by sulphuric acid. Lime, strontian, and protoxide of lead, could probably be separated from boracic acid in the same manner as from arsenic and phosphoric acids (pages 205 and 258).

Decomposition of Borates by Fluor Spar or Hydrofluoric Acid.—There is, however, a method of separating boracic acid from all fixed bases, whose borates are decomposable by concentrated sulphuric acid; and this is the case with the greater part of the borates. According to this method, first described by ARFVEDSON (*Vetenskaps Academiens Handlingar*, 1822, p. 93), the operator proceeds as follows: A weighed quantity of the borate is finely pulverised and mixed, in a platinum crucible, or platinum capsule, with three or four times its weight of finely pulverised fluor spar. The fluor spar must be extremely pure, and quite free from silicic acid. So much concentrated sulphuric acid is then poured over the mixture, that when it is stirred with a platinum spatula, a thick pap is produced. The whole is then heated, and finally is ignited until no more acid vapours are disengaged. The boracic acid is thereby converted into fluoboric gas, which entirely flies off; and solution is evaporated to dryness on the water bath. The quantity of boracic acid which volatilizes during this evaporation is, according to C. G. GMELIN, so small, that it may be quite neglected. The silicic acid is separated from the dry mass in the usual manner. The solution filtered from the silicic acid is mixed with an excess of a solution of carbonate of ammonia, which precipitates the barytes. The solution filtered from this precipitate is evaporated to dryness, and the dry residue is exposed to a gradually-raised heat till it becomes just red-hot. No boracic acid is lost by this ignition, because it does not exist free in the solution, but is combined with ammonia; and, because, secondly, no mixture of acid and aqueous vapour flies off during the ignition, as is the case when sulphate of ammonia is ignited. It is with this object in view, that the barytes is precipitated by carbonate of ammonia instead of by sulphuric acid. The dry residue is weighed after ignition. It is then treated with alcohol and a little muriatic acid. The alcohol is inflamed, and allowed to burn away. This operation is repeated until the edges of the flame no longer exhibit the least tinge of green. By this process, the whole quantity of the boracic acid is got rid off; although contained in the solution as borate of ammonia, it is converted during the ignition into free boracic acid. The residue is now once more ignited and weighed, and the quantity of the boracic acid is indicated by the loss of weight.

Another method which has been recommended by C. G. GMELIN, for the estimation of the boracic acid in these compounds, is the following: The pulverised mineral is ignited with carbonate of soda, and the ignited mass is treated with water. The solution is digested with a solution of carbonate of ammonia, which precipitates the small portions of alumina and silicic acid, which the water had dissolved. The solution is then evaporated to dryness, the dry mass is treated with sulphuric acid, and the boracic acid is dissolved by digestion with alcohol. Finally, the solution is saturated with ammonia, and the residue, which consists of boracic acid, is ignited and weighed.

compound contains both boracic acid and silicic acid, and can still be decomposed by acids, it is possible, on submitting it to analysis in the last-mentioned method, to determine merely the common weight of the two acids, since both silicium and boron are carried off by fluorine. A new portion of the compound must therefore be employed to effect the estimation of the silicic acid. With this view, the compound is decomposed by muriatic acid, upon which the silicic acid remains undissolved, and can be weighed. It is better, however, to evaporate the muriatic acid solution to dryness, to moisten the dry mass with muriatic acid, and, after some time, to add sufficient water to dissolve it; the whole of the silicic acid then remains undissolved.

Separation of Boracic Acid from Silicic Acid and Water: Analysis of Datholite and Botryolite.—If a compound which contains boracic acid and silicic acid, contains water also, as, for example, is the case with the minerals called Datholite and Botryolite, then a third portion of the compound must be analysed for the express purpose of estimating the water. To this end, it is only necessary to ignite the compound in a platinum crucible; the loss of weight indicates the quantity of water.

Analyses of the Silicates which contain Boracic Acid, and cannot be decomposed by Acids.—The quantitative estimation of boracic acid is very difficult to be effected, when it occurs in silicates which are indecomposable by acids. The estimation is the more difficult, when the relative quantity of the boracic acid is, as it commonly happens to be, very small. Boracic acid occurs in nature, under these circumstances, in Axinite and in the Tourmalines. In the analysis of these compounds, the best result which can be obtained is one that approaches the truth; complete accuracy is not attainable. The estimation of the boracic acid in the Tourmalines, has been effected by C. G. GMELIN (POGGENDORFF'S Annalen, T. IX. p. 175) by the process which follows: The finely-levigated powder is mingled with carbonate of barytes, and the mixture is strongly ignited. The ignited mass is then treated with exactly so much muriatic acid as is requisite to decompose it, and the acid solution is evaporated to dryness on the water bath. The quantity of boracic acid which volatilizes during this evaporation is, according to C. G. Gmelin, so small, that it may be quite neglected. The silicic acid is separated from the dry mass in the usual manner. The solution filtered from the silicic acid is mixed with an excess of a solution of carbonate of ammonia, which precipitates the barytes. The solution filtered from this precipitate is evaporated to dryness, and the dry residue is exposed to a gradually-raised heat till it becomes just red-hot. No boracic acid is lost by this ignition, because it does not exist free in the solution, but is combined with ammonia; and, because, secondly, no mixture of acid and aqueous vapour flies off during the ignition, as is the case when sulphate of ammonia is ignited. It is with this object in view, that the barytes is precipitated by carbonate of ammonia instead of by sulphuric acid. The dry residue is weighed after ignition. It is then treated with alcohol and a little muriatic acid. The alcohol is inflamed, and allowed to burn away. This operation is repeated until the edges of the flame no longer exhibit the least tinge of green. By this process, the whole quantity of the boracic acid is got rid off; although contained in the solution as borate of ammonia, it is converted during the ignition into free boracic acid. The residue is now once more ignited and weighed, and the quantity of the boracic acid is indicated by the loss of weight.

Another method which has been recommended by C. G. Gmelin, for the estimation of the boracic acid in these compounds, is the following: The pulverised mineral is ignited with carbonate of soda, and the ignited mass is treated with water. The solution is digested with a solution of carbonate of ammonia, which precipitates the small portions of alumina and silicic acid, which the water had dissolved. The solution is then evaporated to dryness, the dry mass is treated with sulphuric acid, and the boracic acid is dissolved by digestion with alcohol. Finally, the solution is saturated with ammonia, and the residue, which consists of boracic acid, is ignited and weighed.

XLVI. FLUORINE.

Decomposition of Fluorides by Sulphuric Acid.—The most accurate method of effecting the quantitative estimation of fluorine, is unquestionably that of expelling it in the state of hydrofluoric acid gas, and then inferring its quantity from the loss of weight. A weighed quantity of the fluoride is treated with concentrated sulphuric acid, and exposed to a continued heat. The fluorine first escapes in the state of hydrofluoric acid gas, and when the heat is increased, the excess of sulphuric acid is expelled. The metal which was combined with the fluorine, remains then behind in the state of sulphate. It is necessary that this experiment be performed in a platinum crucible, and that no vessel be employed of which silicic acid is a component part. From the weight of the resulting sulphate the quantity of the metal in the base can readily be calculated. The quantity of the fluorine is then found from the loss. When the fluorine is combined with more than one metal, the compound is still decomposed by sulphuric acid; but in that case, the resulting sulphates must be submitted to a farther examination, in order that the respective quantities of the different metals may be determined.

Estimation of the Water of Crystallisation in Fluorides.—When a fluoride contains water of crystallisation, it is possible, in many cases, to determine the quantity of the water from the loss of weight experienced on exposing a weighed quantity of the compound to ignition. In many cases, however, it happens that the simultaneous action of the air and the water effects a partial decomposition of the fluoride, the consequence of which is, that the vaporised water carries away with it a portion of the fluorine, in the state of hydrofluoric acid gas. To prevent this accident, and to determine the quantity of the water of crystallisation in a fluoride with great accuracy, the compound is mingled, in a little glass retort, with about six times its weight of finely-pulverised and recently-ignited protoxide of lead; the mixture is covered with a little protoxide of lead, and the whole is then ignited: the water goes away in this case, unaccompanied by the slightest quantity of acid. The retort is first weighed empty; it is weighed again when the fluoride for examination has been inserted; after the admixture of the protoxide of lead it is once more weighed. The retort is then ignited, and allowed to cool. Upon being then weighed, the loss which is experienced indicates the quantity of water. It is necessary to ignite the mixture in a retort, because even the fluoride of lead is partially decomposed when ignited in the open air. —**Berzelius** has invariably made use of this method, in the estimation of the water of crystallisation of the fluorides.

Separation of Fluorides from Hydrofluoric Acid.—When a compound of fluorine with a metal, which contains also hydrofluoric acid, is to be analysed, the quantity of the hydrofluoric acid can be determined, in a great number of cases, from the loss of weight experienced when a weighed portion of the compound is heated to redness in a platinum crucible. The fixed fluoride alone remains behind. But, since the remaining fluoride is liable, in a great number of cases, to be partially decomposed by ignition in the open air, it is proper, with **Berzelius**, to determine, in most cases, the quantity of the hydrofluoric acid, by mixing the compound with six times its weight of fine-pulverised and recently-ignited protoxide of lead, and then igniting the mixture. When thus treated, the hydrogen of the hydrofluoric acid and the oxygen of the protoxide of lead, produce water which passes away unaccompanied by any acid. That the quantity of this water may be determined, the operator proceeds exactly in the same manner as in the determination of the water of crystallisation of the fluorides. From the quantity of the volatilized water, the quantity of the hydrofluoric acid in the compound can be easily reckoned.—If another portion of the compound be then analysed by decomposition with concentrated sulphuric acid, the weight of the resulting sulphate indicates the common weight of the fluorine and hydrofluoric acid. It is easy to reckon from the above results, what must be the separate weight of the fluorine.

When a compound which contains a fluoride with hydrofluoric acid, contains water of crystallisation also, then the water which is expelled when the compound is ignited with protoxide of lead, consists both of the water of crystallisation of the compound, and of the water produced by the combination of the hydrogen of the hydrofluoric acid with the oxygen of the protoxide of lead. But the respective quantities of these two portions of water must be determined. The operator decomposes another portion of the compound by sulphuric acid, and determines from the weight of the sulphate, the common weight of the fluorine, the hydrofluoric acid, and the water of crystallisation. He then decomposes by sulphuric acid, the mass produced by igniting the compound with protoxide of lead. This analysis makes known the quantity of fluorine contained both in the fluoride and the hydrofluoric acid.

Estimation of Fluorine in Solutions.—It is more difficult to determine the quantity of fluorine in a compound which is dissolved in water. When the compound is not dissolved by the help of a foreign acid, but exists in solution in virtue of the presence of free hydrofluoric acid, it may be decomposed, if the nature of the compound admit of it, by boiling with carbonated or caustic potash. The excess of potash is afterwards saturated by an acid, the solution is then made ammoniacal, and the whole quantity of the fluorine in the resulting fluoride of potassium, is precipitated as fluoride of calcium by the solution of a salt of lime. The quantity of the fluorine can be calculated from the weight of the precipitated fluoride of calcium. A dissolved fluoride, such as is here spoken of, can very seldom be presented for analysis; the precautions which are necessary to be taken in the performance of the experiment, will be, however, circumstantially described hereafter.

Separation of Fluorine from Boron.—The compound of fluorine with boron, and the compounds of fluoride of boron with fluorides of metals, cannot be quantitatively analysed without much difficulty. When they are decomposed in the same manner as the fluorides, namely, by sulphuric acid aided by heat, one can determine from the weight of the resulting sulphates, what is the common weight of the fluoride of boron and fluorine, which were combined with the metals of the resulting oxides. If the compound contain water of crystallisation, it must be estimated by igniting the compound with protoxide of lead, in the same manner as in the case of the fluorides. It is impossible to succeed in decomposing these compounds by treatment with a solution of carbonated or caustic alcali. When they are heated in a retort, the metallic fluoride remains behind, the fluoride of boron flies away. The quantity of the fixed fluoride might then be determined, and the composition of the compound be therefrom calculated; but it is often extremely difficult to effect the entire decomposition of the compound by heating it in the manner alluded to.

Separation of Fluorine from Silicium.—The compound of fluorine with silicium, but more particularly the compounds which fluoride of silicium produces with fluorides of metals, can be more easily analysed than those in which boron is present. When a solution of fluoride of silicium in water is to be analysed, the operator, according to BERZELIUS (POGGENDORFF'S Annalen, T. I. p. 173), can best effect his purpose by the following process: A solution of carbonate of soda is added to the acid solution as long as it produces effervescence; a precipitate is thereby produced, which is the sparingly soluble fluoride of silicium and sodium. This is filtered upon a weighed filter, and edulcorated. The fluoride of silicium and sodium is then dried in a weighed platinum crucible, and in such a manner that the portion of the dissolved salt which has penetrated through the paper of the filter, cannot be lost. The weight of the double salt is then determined, and the respective quantities of the silicium and fluorine are then calculated. The solution which was saturated with soda, is now supersaturated with carbonate of soda, and is mixed with a solution of carbonate of zinc in caustic ammonia. The mixture is then evaporated nearly to dryness. The oxide of zinc combines with the silicic acid and forms a silicate which, when the mass is treated with warm water, remains behind undissolved. It can be washed with water, without losing any thing by solution. This silicate of zinc is afterwards decomposed by nitric acid, and the solution is evaporated to dryness, to render the silicic acid completely insoluble. The dry mass is then treated with acidulated water. The nitrate of zinc dissolves, while the silicic acid remains undissolved; it is filtered, washed, ignited, and weighed. From the weight of the silicic acid, the quantity of the silicium is calculated.—The alcaline solution filtered from the silicate of zinc, and which still contains fluoride of sodium and carbonate of soda, is now saturated with acetic acid, but without being brought to a complete state of neutrality, lest it should occasion a loss of hydrofluoric acid by volatilization. The solution is thereupon cautiously evaporated to dryness, and the dry mass is treated with a mixture of alcohol and acetic acid. The small portion of carbonate of soda, which, in consequence of the incomplete saturation of the alcaline solution by acetic acid, still remains in the dry mass, is thus converted into acetate of soda. The entire quantity of the acetate of soda then dissolves in the alcohol, while the fluoride of sodium remains undissolved. It is filtered, edulcorated with alcohol, dried, ignited, and weighed. From the weight of the fluoride of sodium, the operator calculates the quantity of fluorine.—The constitution of the aqueous solution of fluoride of silicium can be calculated from the results afforded by the above experiments.

If the analyst desires to effect a quantitative estimation of the gaseous compound of fluorine and silicium, he must conduct the gas into water, whereupon a deposition of silicic acid takes place. The gas may be continually passed into the water, until the pasty condition of the solution, produced by the separation of the silicic acid, prevents the absorption of any more gas. It is necessary, that the tube which conducts the gas do not come into contact with the water, otherwise it can readily become stopped. The absorption of the gas is promoted by frequently agitating the liquid. The pasty solution is diluted with water, and the precipitated silicic acid is filtered, and washed with water until the filtered liquor ceases to redden litmus paper. When the silicic acid has been properly edulcorated, it is completely freed from hydrofluoric acid. It is then dried, ignited, and weighed.. The solution filtered from the silicic acid, is treated in the manner which has been described above.

Separation of Fluoride of Silicium from Fluorides of Metals.—The compounds which are formed by the combination of fluoride of silicium with the fluorides of metals, can be analysed in different ways, when they are in a dry state. If they are treated with sulphuric acid and heated, and the excess of sulphuric acid is finally expelled by the application of a strong heat, the whole of the fluorine and silicium is expelled, as fluoride of silicium, and the metal of the fluoride remains behind in the state of sulphate. Most of these compounds are decomposed very rapidly when treated with sulphuric acid, while an abundant discharge of fluosilicic gas takes place. Some of them, however, as, for example, the fluoride of silicium and calcium, and the fluoride of silicium and barium, are not attacked unless the acid be assisted by heat.—The weight of the resulting sulphate is determined, and the quantity of the metal is calculated. From this, the whole composition of the compound can be learned, provided it contained no water of crystallisation.

The compounds of fluoride of silicium with fluorides of metals, can also be analysed, when in a dry state, by ignition. Gaseous fluoride of silicium escapes, while the metallic fluoride remains behind. The composition of the compound can then be reckoned from the weight of the metallic fluoride, supposing that no water of crystallisation was present. It requires, however, a long-continued heat, to expel the whole of the fluoride of silicium. And if the compound be ignited in free air, the remaining metallic fluoride contains free silicic acid, because the slightest trace of moisture in the air is sufficient to precipitate silicic acid from the fluoride of silicium; and the precipitated silicic acid is immediately dissolved by the melted metallic fluoride. This occurs in a more considerable degree when the experiment is performed in an open platinum crucible heated over a spirit lamp, since the burning of the alcohol gives rise to the production of water. BER-

ZELIUS (POGGENDORFF'S Annalen, T. I. p. 189), took the following method of avoiding this inconvenience: Whenever the resulting metallic fluoride was to be weighed, with a view of calculating from its weight the composition of the compound, he placed three covered crucibles within one another, and heated them in a charcoal fire; the compound for examination being placed in the innermost crucible. The silicic acid then settled in a thick crust on the inner side of the outer crucible.

If the compounds of fluoride of silicium with fluorides of metals contain water of crystallisation, its quantity must be determined by an experiment with protoxide of lead. A weighed quantity of the compound is mixed very accurately, in a little distilling apparatus of glass, with six times its weight of finely-pulverised and recently-ignited protoxide of lead; and the mixture is covered with a stratum of protoxide of lead. The whole is thereupon exposed to heat, but the temperature must never be allowed to approach to ignition. The mixture fuses together, and pure water passes off. When the little retort has been weighed, the quantity of the water of crystallisation is ascertained from the loss of weight occasioned by the ignition.

When the compounds of fluoride of silicium with fluorides of metals are in solution, the composition must be determined by decomposing the dissolved compound by a solution of carbonate of soda. It is proper to boil the solution with an excess of the carbonate of soda, by which all these compounds are decomposed. Carbonic acid is disengaged, and fluoride of sodium is formed; while the metal which was combined with the fluorine becomes oxidised, and, if it be insoluble in a solution of carbonate of soda, combines with the silicic acid, and is precipitated. But even when the oxide is soluble in ammonia, the addition of ammonia does not precipitate silicic acid alone, but the silicated oxide. If, on the contrary, the fluorine be combined with an alcaline metal, for example, with sodium, the solution is very slightly supersaturated with carbonate of soda, and a solution of oxide of zinc in ammonia is added as long as it produces a precipitate. After the precipitate is all thrown down, a slight excess of the solution of oxide of zinc in ammonia is added, and the whole is then evaporated until all the ammonia is expelled. The precipitated silicate of zinc is then washed with water, and is afterwards decomposed by nitric acid. When the decomposition is completed, the solution is evaporated to dryness, the dry mass is moistened with nitric acid, and afterwards treated with water. The silicic acid then remains undissolved. It is filtered, dried, ignited, and weighed.—The alcaline solution filtered from the silicate of zinc, is slightly evaporated, upon which the fluoride of sodium shoots into crystals. The supernatant liquid is supersaturated with acetic acid, and mixed with alcohol; the separated fluoride of sodium is then washed with alcohol, dried, ignited, and weighed. From the weight of the resulting fluoride of sodium, the operator calculates the quantity of the fluorine. The quantity of the alcaline metal must now be calculated from the weight of the silicic acid and fluoride of sodium obtained, since it is impossible to estimate it, in consequence of the addition of alcali as a reagent. Yet it is possible to determine the quantity of the alcaline metal experimentally, provided another operation be performed. A different portion of the solution for analysis must be evaporated to dryness, and the dry fluoride of silicium and metal be decomposed by sulphuric acid. The quantity of the metal can then be reckoned from the weight of the sulphate.—If the solution, instead of fluoride of sodium, contains fluoride of potassium, the decomposition is effected by a solution of carbonate of potash; in other respects the operation is perfectly similar to the above.

If the solution contains a compound of fluoride of silicium with the fluoride of a metal whose oxide is an earth or metallic oxide, and not an alcali, then the operator, after the decomposition by carbonate of soda, first determines, in the manner above described, the quantity of the resulting fluoride of sodium, and afterwards decomposes the silicated oxide by an acid, and determines the respective quantities of the silicic acid and the oxide.

Separation of Fluorides from Silicates.—Compounds containing a metallic fluoride in combination with one or more silicated oxides, which are a description of compounds that occur in nature, can be decomposed, in quantitative examinations, by carbonate of soda. If the compound for analysis be of such a description that it cannot be decomposed by muriatic acid in the cold, then, according to the instructions of BERZELIUS (SCHWEIGGER'S *Jahr. der Chemie*, T. XVI. p. 426), it is levigated and dried, and a weighed quantity of it is mixed, in a platinum crucible, with four times its weight of carbonate of soda, and is then subjected for a considerable time to a full red heat. After cooling, the mass is taken from the crucible and softened with water. The insoluble matter is separated by filtration and washed with water, until that which passes through the filter no longer acts alcaline on litmus paper. It is impossible to edulcorate the insoluble matter so completely, that a few drops of the last filtered water, if evaporated to dryness on a platinum spatula, shall leave no residue. The filtered solution, which, besides fluoride of sodium and the excess of carbonate of soda, contains traces of silicic acid, and even of alumina, if the compound contained this substance, is now mixed with carbonate of ammonia. A slight precipitate is then produced, the quantity of which is commonly slightly increased when the solution is evaporated to a small bulk. The precipitate is collected upon the smallest possible filter, and is washed with water. In the next place, this precipitate, as well as the substance which remained undissolved by water, is treated with muriatic acid, which effects an easy and perfect decomposition. When concentrated acid is employed, the silicic acid commonly separates in the form of a jelly. The whole is thereupon evaporated to perfect dryness; the dry mass, after cooling, is moistened in an uniform manner, as has been often repeated, with muriatic acid. After some time, water is added, and the silicic acid, which then remains undissolved, is filtered, washed, dried, ignited, and weighed. The solution, filtered from the silicic acid, now contains all the bases which were contained in the substance submitted to analysis, and all dissolved in muriatic acid. The estimation of these bases is effected by processes which have been already described.

The quantity of the fluoride of sodium in the alcaline solution, which, besides this, contains an excess of carbonate of soda, could be determined according to the method which has been described above, namely, by saturating the solution with acetic acid, and separating the acetate of soda from the fluoride of sodium, by means of alcohol. When, however, the quantity of the metallic fluoride contained in the compound submitted to analysis, is very small, it is better to make use of another process, which has likewise been given by BERZELIUS (SCHWEIGGER'S *Jahrbuch der Chemie*, T. XVI. p. 427). The alcaline solution is evaporated to a sufficiently small volume, and is then cautiously supersaturated with muriatic acid. This operation dare be performed only in a capsule of silver, or what is better, of platinum; and the mixture must be stirred only with a spatula of silver or platinum. The vessel must be loosely covered with filtering paper, and allowed to repose for twenty-four hours, without warming the solution; in the course of that time, the carbonic acid is wholly driven out of the liquid. That the operator may be quite satisfied, that the carbonic acid is entirely expelled from the acid liquor, he may place the vessel on a stove, which must, however, be raised to but a very moderate heat. The temperature dare not rise above +86° F. The solution, still remaining in the metallic capsule, is thereupon slightly supersaturated with caustic ammonia, and is poured into a glass flask which can be closed air-tight with a cork. A solution of chloride of calcium is then added, and the flask is immediately closed. The precipitate which falls down is fluoride of calcium. The reason that the carbonic acid is first carefully expelled from the solution, and that the presence of atmospheric air is sought to be avoided after the addition of the chloride of calcium, is, that the precipitated fluoride of calcium would otherwise be contaminated by carbonate of lime. When the fluoride of calcium has fully subsided, the supernatant liquor is poured out of the flask; the operator then pours on the precipitate a quantity of water that has been previously boiled to free it from air, and again closes the flask. As soon as the fluoride of calcium has again subsided, the liquid is filtered; the precipitate is then washed, dried, ignited, and weighed. From the weight of the resulting fluoride of calcium, the quantity of the fluorine in the compound is calculated.—It is always necessary to examine whether the ignited fluoride of calcium be pure or not. It must be moistened with water, in the platinum crucible, and then treated with muriatic or acetic acid; the object of this is, to ascertain whether carbonic acid be present. If a strong effervescence is observed, the fluoride of calcium which has been treated with muriatic or acetic acid, must be mixed with alcohol. The insoluble matter is then washed with alcohol, and again dried, ignited, and weighed. By proceeding thus, the operator at length ascertains the true quantity of fluorine in the compound.—Sometimes the precipitated fluoride of calcium can contain a little silicic acid. A proof of the absence of silicic acid is afforded, when the suspected fluoride of calcium, upon being moistened, after ignition, with pure hydrofluoric acid, does not produce the least heat; for the smallest quantity of silicic acid produces heat when thus treated. This test is given by BERZELIUS (POGGENDORFF'S Annalen, T. I. p. 39). When fluor spar is tested in this manner, for silicic acid, it must previously be pulverised.

When fluoride of calcium is precipitated from the ammoniacal solution by means of a solution of chloride of calcium, the precipitate often assumes the form of a jelly, which is so transparent, that at first the operator imagines only a very inconsiderable precipitate to have been produced. When looked at through the glass, it has an opalescent appearance, with somewhat of a reddish colour. This jelly cannot be washed, because it stops the pores of the paper. Its production takes place more particularly, when the solution to which the chloride of calcium is added, contains a very inconsiderable excess of ammonia. A greater addition of ammonia precipitates this fluoride of calcium completely.

When the compound submitted to analysis contains a great quantity of lime, or rather when it consists of fluorine combined with calcium, it is not possible to obtain the entire quantity of fluorine, by fusing the compound with carbonate of soda. It appears as if carbonate of soda could not effect a complete decomposition of fluoride of calcium.

By the above process, however, it is possible to decompose those compounds only which do not contain too much silicic acid. The compounds in which the silicic acid of the silicates in combination with metallic fluorides, contains the same quantity of oxygen as the bases (ein drittel kieselsauren Basen), or even twice as much oxygen as the bases (zwei drittel kieselsauren Basen), can be completely decomposed by carbonate of soda, since these silicates are insoluble in a solution of carbonate of soda. But when the silicate is neutral, that is to say, when the silicic acid contains three times as much oxygen as the base combined with it, then a portion of the silicic acid is dissolved by the carbonated alcali; and when the ignited mass is afterwards treated with water, a solution is obtained which contains not only fluoride of sodium and carbonate of soda, but also silicate of soda; while the undissolved matter consists of the bases in combination with the greater part of the silicic acid. To precipitate the silicic acid from the dissolved silicate of soda, a solution of carbonate of zinc in ammonia must be added to the solution. The silicic acid is thereby thrown down as silicate of zinc. The estimation of the bases now becomes more difficult, on account of the necessity for separating the oxide of zinc. It is possible, however, to analyse separately the silicated bases which remain undissolved when the ignited mass is treated with water, and afterwards to estimate the silicic acid contained in the silicate of zinc, by a separate decomposition by nitric acid. This simplifies the analysis.

Of the compounds which occur in nature, containing both silicated oxides and metallic fluorides, and which are lecomposable by muriatic acid, that which contains the atest quantity of fluorine is the topas. Much smaller quantities of this element are contained in the micas, the amphiboles, and in some varieties of scapolite.

When a compound containing a silicated oxide with a metallic fluoride, can be very easily decomposed by muriatic acid, the decomposition of the compound by this acid must be effected in the cold. The slightest application of external heat must be carefully avoided, because it can lead to the production and volatilization of fluoride of silicium. If the solution, produced by the decomposition of the compound by muriatic acid, be evaporated to dryness, the subsequent analysis commonly affords no signs of fluorine, the reason of which is, that the whole of the fluorine is driven away, in the state of fluosilicic gas, during the evaporation of the solution. In consequence of this circumstance, it has very frequently happened, that the presence of a small quantity of a fluoride in minerals, as, for example, in apophyllite, has been quite overlooked in analyses.

When the quantity of the metallic fluoride contained in the compound for analysis, is not very considerable, which is always the case with the compounds of this description which occur in nature, the compound is decomposed in the cold by muriatic acid, in a platinum vessel, and the silicic acid which remains undissolved is first separated. If the compound contains neither alumina nor peroxide of iron, nor indeed any basic constituent which can be precipitated by ammonia, but has no other base than lime, the solution is then treated with ammonia, which precipitates a compound of fluoride of calcium with silicate of lime. This compound is washed, dried, ignited, and weighed: it contains three atoms of fluoride of calcium with one atom of silicate of lime, in which the oxygen of the acid is twice as much as the oxygen of the base (zwei drittel kieselsaure Kalkerde). Berzelius obtained this compound by the above process, in his analysis of the Apophyllite. It was considered by chemists who had previously analysed that mineral, to be alumina.—If, however, the compound contains other constituents which can be precipitated by ammonia, the solution separated from the silicic acid must be supersaturated by a solution of carbonate of soda, and therewith be digested or boiled. Fluoride of sodium and carbonate of soda then remain in solution, while the other constituents of the compound are generally precipitated. The quantity of the fluorine is then determined in the manner described above.

Separation of Fluorides from Phosphates.—The fluorides which occur in nature are very often found in combination with phosphates. Indeed, phosphoric acid so generally occurs in the fluorides, that, when fluorine has been detected in a native compound, the operator must never neglect to examine the compound for phosphoric acid, nor, when phosphoric acid has been detected, to examine it for fluorine. In some of the fluorides which occur in nature, and which have been considered to be very pure, BERZELIUS has discovered small quantities of phosphoric acid. This is, for example, the case with fluor spar (POGGENDORFF'S Ann. T. I. p. 37). On the other hand, small quantities of metallic fluorides have been found in the phosphates; as, for example, in Wavellite and in bones.

The methods of separating phosphoric acid from the fluorides depend upon the nature of the other constituents in the compound. If a compound is indecomposable by acids, and contains a very small quantity of fluorine and phosphoric acid, and a very considerable quantity of silicated oxides, it is ignited with carbonate of soda, and the ignited mass is then treated with water, in the manner which has been described above. The alcaline solution, filtered from the insoluble matter, contains fluoride of sodium, phosphate of soda, and carbonate of soda. The method of examining this solution is similar to that which has just been described, at page 342. The solution is rendered ammoniacal, and is mixed, in a glass flask which can be closed air-tight, with a solution of chloride of calcium. A precipitate is then obtained, which consists of phosphate of lime and fluoride of calcium. This is washed, dried, ignited in a platinum crucible, and then weighed. The best method of quantitatively separating the two compounds is that which has been given by BERZELIUS (GILBERT'S Ann. der Physik, T. LXXIV. p. 142). While the mixture is still in the platinum crucible in which it was ignited and weighed, it is treated with concentrated sulphuric acid. If this produces no effervescence in the cold, the mixture is free from silicic acid and from carbonate of lime. The crucible is then heated, until all the fluorine is expelled in the state of hydrofluoric acid gas. A small glass plate is held from time to time over the crucible, and when it is no longer attacked by the vapours which arise, it is a sign that the fluorine has been entirely driven away. The acid mass which remains behind is then treated with a large quantity of water, which dissolves the excess of sulphuric acid, and the sulphate of lime resulting from the decomposition of the fluoride of calcium; while the phosphate of lime remains undissolved. The solution is saturated with ammonia, and the lime is precipitated by oxalate of ammonia. The resulting oxalate of lime is converted, by the process described at page 17, into carbonate of lime, which is to be weighed. From this weight, the quantity of the fluoride of calcium is calculated.—The operator then determines the weight of the undissolved phosphate of lime, and afterwards submits it to the operation described at page 263, for the purpose of ascertaining its quantity of phosphoric acid.

When a compound of this description can be decomposed by muriatic acid, the decomposition must be thus effected, in a platinum vessel, and in the cold; the precipitated silicic acid must then be separated by filtration. If the solution contains neither alumina, peroxide of iron, nor any other basic constituent capable of precipitation by ammonia, but merely lime as the base, then upon being treated with ammonia, it yields a precipitate consisting of fluoride of calcium, silicate of lime, and phosphate of lime. The weighed precipitate is treated with sulphuric acid, in a platinum crucible, and is heated to expel the fluosilicic gas. The mass is thereupon treated with water, which dissolves the excess of sulphuric acid and the resulting sulphate of lime. The lime is then precipitated and estimated in the manner described above. From the weight obtained, the operator calculates how much fluoride of calcium and silicate of lime were contained in the precipitate thrown down by ammonia. The relative proportions of these two compounds in the precipitate have been stated above. The quantity of the phosphoric acid existing in the undissolved phosphate of lime has also to be estimated.

By this process, however, only those compounds can be examined which contain but a very small quantity of phosphoric acid and fluorine, and both of these substances merely as accidental ingredients. When the quantity of the phosphoric acid is more considerable, it is impossible to precipitate most bases from its solution by carbonate of soda, in such a manner that they shall contain no more phosphoric acid. In this case, the compound must be ignited with carbonate of soda.

This method of analysis must also be employed when the compound contains no silicic acid. But if alumina be among the constituents, as it is in Wavellite, the compound must be ignited with carbonate of soda and silicic acid, in the manner which has been described at page 256. Upon treating the ignited mass with water, a solution is obtained holding carbonate of soda, fluoride of sodium, and phosphate of soda. The respective quantities of the fluorine and phosphoric acid are then to be estimated by the methods already described.

Separation of Fluorides from Sulphates.—Some of the fluorides, fluor spar, for example, occur in nature, in combination with sulphates. When the sulphate is Heavy spar, it is only necessary to treat the substance, in a platinum vessel, with muriatic acid; thereupon, the fluor spar dissolves in the diluted solution, while the heavy spar remains undissolved, and, after dilution, can be collected and weighed. The solution of fluor spar in muriatic acid can be mixed with sulphuric acid, and evaporated to dryness. Sulphate of lime is then obtained, and can be weighed. The quantity of the fluor spar is calculated.—If the sulphates dissolve with the fluorides in muriatic acid and water, the diluted acid solution is mixed, in a platinum vessel, with a solution of chloride of barium. The proportion of the sulphuric acid can then be readily ascertained. The bases are estimated by another experiment, in which a quantity of the compound is treated with sulphuric acid, and the whole of the bases are converted into sulphates.

XLVII. CHLORINE.

Precipitation of Chlorine by Nitrate of Silver.—The quantitative estimation of chlorine when combined with metals or hydrogen, is effected as follows: The compound is dissolved in water, if soluble therein, and the solution is mixed with a solution of nitrate of silver. This produces a precipitate of chloride of silver, from the weight of which, the quantity of the chlorine is calculated. The precautionary measures which are necessary to be employed in the quantitative analysis of chlorine, and particularly in the fusion of the chloride of silver, have been fully detailed at p. 115.

It is proper, and in a great number of cases absolutely necessary, to add a small quantity of acid to the water in which the chloride is dissolved, before pouring in the solution of oxide of silver. Diluted nitric acid is commonly employed for this purpose. The use of this acid can produce no bad consequences, if the solution of the chloride be pretty dilute, and the nitric acid not very concentrated.

When the chlorine contained in a soluble chloride has been precipitated by a solution of silver, in the state of chloride of silver, the next operation is to estimate the quantity of the metal which was previously in combination with the chlorine, and which now exists in the filtered solution in the state of nitrate of oxide. This estimation is performed according to methods which have been circumstantially described in the foregoing sections. Before, however, the metallic oxides can be separated, it is necessary, in most cases, to precipitate the excess of oxide of silver from the solution. This is done by adding muriatic acid to the liquor filtered from the chloride of silver. The solution is separated by the filter from this new portion of chloride of silver, and the metallic oxides can then be estimated.

Analysis of Volatile Chlorides: Separation from Phosphorus, Sulphur, Selenium, Arsenic, Chromium, Titanium, Antimony, Tin, &c.—When very volatile chlorides, as, for example, the compounds of chlorine with phosphorus, sulphur, selenium, arsenic, chromium, titanium, antimony, tin, &c. are to be analysed, they must likewise be dissolved in water. Most of these, even when they are decomposed by water, dissolve in it, and give a clear solution. A few of them only, as, for example, the compounds of chlorine with sulphur and selenium, afford a deposite when treated with water, which in these cases is sulphur or selenium. Whenever these volatile compounds dissolve completely in water, even though it be in consequence of decomposition, the operator treats the solution exactly in the same manner as the solution of chlorides which dissolve in water without decomposition. The solution is commonly mixed with a little nitric acid, and the chlorine is precipitated by a solution of nitrate of silver. The solution is filtered; the excess of oxide of silver is precipitated by muriatic acid; the solution is again filtered, and the substance which was combined with chlorine in the compound submitted to analysis, can then be estimated.—It is necessary, however, if we desire to prevent losses, to take notice of the difficulties which attend, not only the weighing of these extremely volatile metallic chlorides, but also their mixture with water. As the volatile chlorides quickly evaporate in the open air, it is necessary, in the first place, to weigh them out of contact with the atmosphere. Particular caution must also be observed in the mixing of these compounds with water, because, in almost all cases, a great deal of heat is disengaged; in consequence of which, a considerable proportion of the resulting muriatic acid can be easily volatilized. A plan must be adopted, therefore, by which these compounds may be weighed and mixed with water without loss. The best way to proceed is as follows: A small glass bulb with a long neck is blown of pretty thin glass. The neck must be terminated by a long and very fine point. When the glass bulb has been weighed, it is exposed to the strongest heat that the thin glass can support without softening. As soon as the air has been thus expelled from its interior, the fine point or neck is plunged into the volatile chloride which is to be analysed; whereupon, in proportion as the glass cools, the volatile chloride ascends into the bulb. When the glass is full of the compound, the fine point is carefully dried, and the weight of the whole is determined. The operator thus learns the quantity of the compound employed in the experiment. The point of the glass bulb must be made so fine that nothing can escape in vapour during the operation of weighing. The operator then places the glass bulb with some water, in a flask which can be closed air-tight by a glass stopple. After closing the flask, he shakes it until the glass bulb is broken. The chloride then mixes with the water, under circumstances in which the loss of the least portion of the chloride or of the resulting muriatic acid, is impossible. When the solution is cold, it is carefully poured out of the flask, so as to leave the fragments of glass behind; and the fragments and the flask are carefully washed with water.

Most of these volatile chlorides are decomposed by water in such a manner, that the hydrogen of the water produces muriatic acid with the chlorine, while the oxygen of the water, by oxidising the body which was previously in combination with the chlorine, gives origin, in most cases, to another acid. This is immediately dissolved, either by the water or the resulting muriatic acid. When the operator knows how much oxygen is contained in the oxide produced by this experiment, it is a very easy matter to reckon the composition of the chloride. But when he is not acquainted with the quantity of oxygen, it is necessary to estimate that of the muriatic acid, by precipitating it as chloride of silver by a solution of oxide of silver. From the weight of this precipitate it is easy to calculate, not only the quantity of the substance which was in combination with the chlorine, and which quantity is inferred from the loss, but also the state of oxidation of the oxide produced; for, the weight of the chloride of silver indicates both the composition of the original chloride, and the quantity of water which would be required to decompose it. Hence the weight of the oxygen can be inferred with ease. In other words, the body which was combined with the chlorine takes up a quantity of oxygen equivalent to the hydrogen which produces muriatic acid by combining with the chlorine; hence, it must follow, that the quantity of oxygen in the resulting oxide must bear the same relation to the quantity of chlorine found by experiment, that one atom of oxygen bears to a double atom of chlorine.

The course of analysis described above is adapted to the examination of most of the chlorides which are soluble in water. In some cases, however, the course of analysis must be different. The methods of examination proper to be employed in various cases, shall be successively treated of.

Separation from Phosphorus, Selenium, Arsenic, &c.—In the analysis of a variety of the chlorides which are soluble in water, it is absolutely necessary to separate, or quantitatively estimate, the resulting oxide or oxygen acid, *before* any attempt is made to precipitate the chlorine from the solution, by means of the solution of silver. This is the case with several of the compounds which are formed by chlorine with powerful electro-negative elements. When these are converted by water into oxides or oxygen acids, it is often the case, that when an excess of the solution of oxide of silver is added to the acid solution, the resulting precipitate not only contains chloride of silver, but a compound of oxide of silver with the new oxide or oxygen acid. The compounds which thus precipitate with the chloride of silver, are sometimes dissolved with great difficulty, sometimes with great ease, by free nitric acid. When the two chlorides of phosphorus, the chloride of selenium which is equivalent to the selenious acid, the chlorides of arsenic, &c. are decomposed by water, it is only necessary to add to the acid solution, either *after*, or, what is better, *before*, the addition of the solution of oxide of silver, a sufficient quantity of nitric acid, to prevent completely the contamination of the precipitated chloride of silver, by phosphate, selenite, arsenite, and arseniate of oxide of silver. Even in the solution of the liquid chloride of phosphorus, which is equivalent in composition to the phosphorous acid, it is sufficient to have added a sufficient quantity of free nitric acid, previous to the addition of the nitrate of silver, to prevent entirely the reduction of the oxide of silver by the resulting phosphorous acid.

Separation from Tin.—In the examination of the compounds of chlorine with titanium, tin, and antimony, it is necessary to operate in another manner. If a solution of oxide of silver be added to a solution of perchloride of tin or perchloride of titanium in water, the precipitate which is produced, not only contains chloride of silver, but a compound of oxide of silver with peroxide of tin or titanic acid. This is the case, even when the solution has been acidulated by nitric acid; and from these extraneous bodies, the chloride of silver cannot be well freed by the sole action of nitric acid.—In consequence of this behaviour, it is necessary to pass through the solution of perchloride of tin, a current of sulphuretted hydrogen gas, which precipitates the peroxide of tin as sulphuret of tin. But the sulphuret of tin which is equivalent to the peroxide of tin is slowly precipitated by sulphuretted hydrogen gas, and requires for its perfect separation, the exposure of the solution to digestion, by which a slight quantity of muriatic acid can easily be volatilized. It is, therefore, indispensable to effect the precipitation and digestion in a flask which can be corked. The whole is allowed to repose for a considerable time, and when the sulphuret of tin has completely subsided, it is filtered, and quantitatively estimated in the manner described at page 162. In the solution filtered from the sulphuret of tin, the whole of the chlorine is to be found. But, as the solution still contains traces of sulphuretted hydrogen, it must, in the first place, be freed from that reagent; because the addition of the solution of nitrate of silver would otherwise precipitate both chloride and sulphuret of silver. To this end, the solution filtered from the sulphuret of tin is mixed with a solution of sulphate of deutoxide of copper. The sulphuretted hydrogen is thereby destroyed, and sulphuret of copper is precipitated. This is separated by filtration, and the solution is then acted on by a solution of nitrate of silver. From the weight of the precipitated chloride of silver, the operator calculates the quantity of chlorine contained in the chloride submitted to analysis.

Separation from Titanium.—The solution of the perchloride of titanium in water is somewhat milky. The milkiness is owing to the presence of a little titanic acid, which of oxygen in the resulting oxide must bear the same relation to the quantity of chlorine found by experiment, that one atom of oxygen bears to a double atom of chlorine.

The course of analysis described above is adapted to the examination of most of the chlorides which are soluble in water. In some cases, however, the course of analysis must be different. The methods of examination proper to be employed in various cases, shall be successively treated of.

Separation from Phosphorus, Selenium, Arsenic, &c.—In the analysis of a variety of the chlorides which are soluble in water, it is absolutely necessary to separate, or quantitatively estimate, the resulting oxide or oxygen acid, *before* any attempt is made to precipitate the chlorine from the solution, by means of the solution of silver. This is the case with several of the compounds which are formed by chlorine with powerful electro-negative elements. When these are converted by water into oxides or oxygen acids, it is often the case, that when an excess of the solution of oxide of silver is added to the acid solution, the resulting precipitate not only contains chloride of silver, but a compound of oxide of silver with the new oxide or oxygen acid. The compounds which thus precipitate with the chloride of silver, are sometimes dissolved with great difficulty, sometimes with great ease, by free nitric acid. When the two chlorides of phosphorus, the chloride of selenium which is equivalent to the selenious acid, the chlorides of arsenic, &c. are decomposed by water, it is only necessary to add to the acid solution, either *after*, or, what is better, *before*, the addition of the solution of oxide of silver, a sufficient quantity of nitric acid, to prevent completely the contamination of the precipitated chloride of silver, by phosphate, selenite, arsenite, and arseniate of oxide of silver. Even in the solution of the liquid chloride of phosphorus, which is equivalent in composition to the phosphorous acid, it is sufficient to have added a sufficient quantity of free nitric acid, previous to the addition of the nitrate of silver, to prevent entirely the reduction of the oxide of silver by the resulting phosphorous acid.

Separation from Tin.—In the examination of the comphurous or selenious acid. In the analysis of the liquid chloride of selenium, the precipitated selenium must be permitted to digest for some time, as it can otherwise retain a portion of chlorine. It must then be filtered on a weighed filter, and weighed. The solution filtered from the selenium contains muriatic acid and selenious acid. The muriatic acid is precipitated by a solution of nitrate of silver, and the excess of oxide of silver is separated by muriatic acid. The selenious acid is then precipitated by a solution of sulphurous acid, in the manner described at page 221.

Separation from Sulphur.—In the decomposition of the chloride of sulphur by water, great care must be taken to provide against the escape of any sulphurous acid. It is, however, better to estimate merely the quantity of the muriatic acid in the solution, to calculate thence the quantity of chlorine, and to infer the quantity of sulphur from the loss. The chloride of sulphur to be analysed, is decomposed by water in a flask provided with a ground-glass stopple, and the solution is allowed to digest for some time in a warm situation. The separated sulphur is at first milky, but it gradually subsides in the form of drops which remain for a long time in a state of fluidity in the cold. These drops contain a little chlorine. When, however, the whole has been allowed to digest for some time, the sulphur becomes solid, particularly if it be stirred with a glass rod. It is then filtered, and nitric acid is added to the filtered solution, which is afterwards precipitated by a solution of nitrate of silver. The addition of nitric acid is necessary, to prevent the reaction of the sulphurous acid on the oxide of silver. The quantity of chlorine is reckoned from the weight of the precipitated chloride of silver.

Analysis of insoluble Chlorides.—Some of the compounds which contain chlorine are insoluble in water, but capable of solution in acids. This is the case with many of the compounds of metallic chlorides with metallic oxides. When a compound of this description is to be analysed, it is first dissolved in an acid, the solution is diluted with water, and then acted on by a solution of silver. The chlorine is thereby precipitated in the same manner as is separated in consequence of the heat produced by the mixture of the perchloride of titanium with water. The first step in the analysis is to precipitate the titanic acid by ammonia. An excess of the precipitant is to be avoided. The glass is then placed in a moderately warm situation, until the solution no longer smells of ammonia. The titanic acid is then filtered. The solution filtered from the titanic acid is acidulated by nitric acid, and mixed with a solution of nitrate of silver, to precipitate the chlorine as chloride of silver.

Separation from Antimony.—When the volatile perchloride of antimony, which is equivalent to antimonic acid, is to be analysed, then the water by which the chloride is to be decomposed, must be previously mixed with such a quantity of tartaric acid, that the solution produced by the decomposition shall remain clear. The first thing to do then, is to precipitate the antimonic acid, in the state of sulphuret of antimony, by a current of sulphuretted hydrogen gas. This precipitate is afterwards examined in the manner described at page 176. The solution filtered from the sulphuret of antimony, is mixed with a small quantity of a solution of sulphate of deutoxide of copper. By this means, the last traces of sulphuretted hydrogen are removed. The solution filtered from the sulphuret of copper, is acted on by nitrate of silver, to separate the chlorine.—The chloride of antimony which is equivalent to the protoxide of antimony, or the solution of that chloride in muriatic acid *(Butyrum Antimonii)*, is analysed in the same manner. In the examination of this compound, less care is required to prevent a loss during its decomposition by water. The operation of weighing and dissolving it in water may be performed in the ordinary manner, and those precautionary measures so necessary to be observed in treating the volatile chlorides, may here be neglected.

Separation from Selenium.—Some of the volatile chlorides do not dissolve completely when decomposed by water. This is the case with the chloride of sulphur, and with the liquid chloride of selenium. When these are decomposed by water, they deposite a portion of sulphur or selenium. Another portion of the sulphur or selenium produces sulissues forth.—It is possible to decompose by this mode of treatment most of the chlorides whose metallic oxides can be converted into metal by being heated in an atmosphere of hydrogen gas. It is only necessary to be observed, that the reduction of the chlorides by hydrogen gas requires a somewhat greater heat than the reduction of the oxides. But of the chlorides which most generally occur, it is only chloride of lead which it is customary to treat in this manner. The reason why chloride of lead is thus decomposed is, that it is so very sparingly soluble in water, that inconveniences arise in bringing it into solution.

Separation from Silver by Fusion with Alcalies.—The decomposition of chloride of silver, with a view to the quantitative estimation of the silver, can be effected by a process different from the above, but not so advantageous. The chloride of silver is mingled, in a little porcelain crucible, with twice its weight of carbonate of soda, or what is better, of a mixture of five parts of carbonate of potash with four parts of carbonate of soda. The whole is then heated over a spirit lamp with circular wick. The silver is thereby completely reduced, under disengagement of carbonic acid gas, even when the alcali does not come into perfect fusion. When effervescence is no longer observable, the porcelain crucible is allowed to become completely cold, and the ignited mass is treated with water. The silver remains undissolved in a state of very fine division. It is filtered, washed, ignited and weighed. This method is employed with much advantage whenever it is not possible to place the fused chloride of silver in the glass bulb. Thus, it is particularly advantageous, when the chloride of silver given in an analysis, has been melted and weighed in a porcelain crucible, and it remains still to be determined whether the chloride of silver be pure or not. The alcaline carbonate is then added to the mass, and the mixture is again ignited in the same crucible. The operator then readily ascertains from the quantity of the resulting silver, whether the chloride of silver employed in the experiment had the proper composition or not.

Separation from Mercury.—To decompose the protochloride of mercury, it is only necessary to digest it with a solution of caustic potash. The solution filtered from the protoxide of mercury, contains the chlorine, in the state of chloride of potassium. The solution is acidulated by nitric acid, and the chlorine is precipitated in the state of chloride of silver, by adding a solution of nitrate of silver. The quantity of the mercury contained in the precipitated protoxide of mercury could be ascertained by various methods; but it is better to estimate the quantity of the mercury, by treating another portion of the protochloride of mercury, previously reduced to a pulverised state, with muriatic acid and protochloride of tin, in the manner described at page 118.

Separation from various Metals, by Sulphuretted Hydrogen Gas.—Several of the chlorides which are insoluble in water and in acids, and which contain metals that can be fully precipitated from their solutions by sulphuretted hydrogen gas, may be analysed as follows: A weighed quantity of the chloride having been finely pulverised, is placed in a flask which can be closed, and after admixture with water, is exposed to a current of sulphuretted hydrogen gas until the gas ceases to be absorbed. The metal is thus converted into a metallic sulphuret which remains undissolved, while the chlorine produces muriatic acid which dissolves in the solution. The sulphuret is separated by filtration, and the filtered solution is mixed with a solution of sulphate of deutoxide of copper. This precipitates the excess of sulphuretted hydrogen, in the state of sulphuret of copper. The precipitate is filtered, and the chlorine is precipitated from the solution, by means of nitrate of silver. The composition of the chloride is then ascertained from the quantities of the metallic sulphuret and chloride of silver.—It is necessary to shake the flask now and then, while the sulphuretted hydrogen gas is being passed into the solution. This serves to bring the particles of the pulverised substance better into contact with the sulphuretted hydrogen gas. If the solution still smells of sulphuretted hydrogen after having been shaken for some time, it is a proof that it is fully saturated with that gas.

Separation from Manganese, Iron, Zinc, and Cobalt.—There is still another method of examining the chlorides which are insoluble in water, a method too, which can be employed in the examination of those chlorides whose metals can only be fully precipitated as sulphurets, from neutral solutions, by soluble sulphurets. This is the case with manganese, iron, zinc, and cobalt. A weighed quantity of the chloride for examination, is treated with bihydrosulphuret of ammonia, or with a solution of sulphuret of barium, or any other soluble sulphuret. The operation is best performed in a flask which can be closed, in order that the whole may be exposed with safety to a very gentle heat, while permitted to digest. When the precipitated metallic sulphuret has been filtered, the solution, which contains muriate of ammonia, or chloride of barium, with the excess of bihydydrosulphuret of ammonia or sulphuret of barium, is cautiously mixed with diluted sulphuric acid, and a solution of sulphate of deutoxide of copper is added, to separate the remaining sulphuretted hydrogen. When the solution has been filtered from the sulphuret of copper, chloride of silver is thrown down by a solution of nitrate of silver. The quantity of chlorine contained in the substance submitted to examination, is calculated from the weight of this last precipitate.

Separation from Carbon.—The compounds of chlorine and carbon which are insoluble in water, are analysed by a process differing from all the preceding. A small weighed portion of the compound is treated with deutoxide of copper in the manner which will be described in the 51st section. The operation produces carbonic acid, from the quantity of which, the operator calculates the weight of the carbon. The quantity of chlorine is learned from the loss of weight.

Decomposition of Chlorides by Sulphuric Acid.—From most of the metallic chlorides which are not volatile, and which have to be examined in a solid state, the chlorine can, generally speaking, be expelled in the same manner as fluorine from the fluorides, that is to say, by treating the compound with concentrated sulphuric acid. Muriatic acid is expelled in the gaseous state, and the quantity of chloride of mercury, it is only necessary to digest it with a solution of caustic potash. The solution filtered from the protoxide of mercury, contains the chlorine, in the state of chloride of potassium. The solution is acidulated by nitric acid, and the chlorine is precipitated in the state of chloride of silver, by adding a solution of nitrate of silver. The quantity of the mercury contained in the precipitated protoxide of mercury could be ascertained by various methods; but it is better to estimate the quantity of the mercury, by treating another portion of the protochloride of mercury, previously reduced to a pulverised state, with muriatic acid and protochloride of tin, in the manner described at page 118.

Separation from various Metals, by Sulphuretted Hydrogen Gas.—Several of the chlorides which are insoluble in water and in acids, and which contain metals that can be fully precipitated from their solutions by sulphuretted hydrogen gas, may be analysed as follows: A weighed quantity of the chloride having been finely pulverised, is placed in a flask which can be closed, and after admixture with water, is exposed to a current of sulphuretted hydrogen gas until the gas ceases to be absorbed. The metal is thus converted into a metallic sulphuret which remains undissolved, while the chlorine produces muriatic acid which dissolves in the solution. The sulphuret is separated by filtration, and the filtered solution is mixed with a solution of sulphate of deutoxide of copper. This precipitates the excess of sulphuretted hydrogen, in the state of sulphuret of copper. The precipitate is filtered, and the chlorine is precipitated from the solution, by means of nitrate of silver. The composition of the chloride is then ascertained from the quantities of the metallic sulphuret and chloride of silver.—It is necessary to shake the flask now and then, while the sulphuretted hydrogen gas is being passed into the solution. This serves to bring the particles of the pulverised substance better into contact with the sulphuretted hydrogen gas. If the solution still smells of sulphuretted hydrogen after having been shaken for some time, it is a proof that it is fully saturated with that gas.

scription which occur in nature are Sodalite, Eudialite, and Pyrosmalite.

When the silicates which contain chlorides cannot be decomposed by acids, they must be ignited with carbonate of alcali. The ignited mass is treated with water, which dissolves the carbonate of alcali with the chloride of potassium or sodium produced by the process. The solution is then supersaturated with nitric acid, and the chlorine is precipitated by a solution of nitrate of silver.

Separation from Fluorine, Arsenic Acid, Phosphoric Acid, and Carbonic Acid.—The analysis of the fluorides as well as of the arseniates, phosphates, and carbonates, which contain chlorides, is performed by dissolving a weighed quantity of the compound, in the cold if possible, in nitric acid. The solution is diluted with water, and mixed with a solution of nitrate of silver. It is proper to employ a particular weighed portion of each of these compounds for the estimation of the chlorine alone. The fluorides must be dissolved in a platinum vessel, and the dilution with water, and precipitation of the chloride of silver by the solution of nitrate of silver, must be effected in the same. When only an extremely small quantity of the fluoride is present, the compound may be decomposed in a glass. Should a compound of this description contain but a very small quantity of the chloride, but at the same time a large quantity of phosphoric acid, which does not admit of being estimated with great accuracy, it is then impossible to determine directly the quantity of the fluorine. This is the case, for example, with several varieties of Apatite. The operator then determines, with two different weighed portions, the respective quantities of the chlorine and the bases, which exist partly as oxides in combination with the phosphoric acid, partly as metals in combination with the fluorine and chlorine. Another portion of the compound is then ignited with an excess of carbonate of soda, and after ignition, is treated with water. The solution so produced contains phosphate of soda and fluoride of sodium, which substances can be analysed in the manner described at page 346.

Quantitative Estimation of Chlorine Gas.—Free chlorine gas cannot be estimated according to bulk, without extreme difficulty; since, as it is absorbed both by water and mercury, neither of these liquids can be employed to confine it in the vessels. The best way to proceed, when free chlorine gas is to be quantitatively estimated, is to lead it, with care, in proportion as it is disengaged, into a solution of ammonia, which has been previously diluted with water. A portion of the ammonia is then decomposed; muriate of ammonia is formed, and remains in solution; while free nitrogen is disengaged as gas. Care must be taken to disengage the chlorine as slowly as possible. This is necessary to ensure the complete decomposition of the ammonia, and to prevent the discharge of chlorine in company with the nitrogen. The ammonia should be poured into a pretty large flask, and this should be closed by a cork having the glass tube passed through it which is to conduct the chlorine into the solution. The cork must not close the flask quite air-tight, but be set in loosely, to allow room for the nitrogen gas to escape. It is necessary that the ammonia be present in excess, in order that no chloride of azote may be produced. When the disengagement of chlorine ceases, all the gas that remains in the flask in which it was produced and in the conducting tubes leading from it, is expelled therefrom by means of carbonic acid gas; the chlorine gas being driven into the solution of ammonia. The method of performing this operation has been described at page 230, in treating of the absorption of sulphuretted hydrogen gas by metallic solutions.—The ammoniacal solution is thereupon acidulated by nitric acid, and the chlorine is precipitated in the state of chloride of silver, by a solution of nitrate of silver.

Quantitative Estimation of the Chlorates.—With respect to the oxides of chlorine and their combinations with bases, it is to be observed that their analysis is often attended by great difficulties. To determine the quantity of the chlorine contained in the acid, and the quantity of the metal contained in the oxide, of a chlorate, it is best to expose a weighed quantity of the chlorate to ignition. It is thus converted into a metallic chloride, while oxygen gas flies away. If the salt contains no water of crystallization, its composition can be easily reckoned from the quantity of the resulting metallic chloride. The quantity of the chloric acid could also be determined from the volume of the oxygen gas which is set at liberty.

Analysis of Chloride of Lime, or Bleaching Powder.—Much more important, in a technical point of view, is the analysis of the chlorites. Compounds which very frequently have to be examined are the solutions of chlorite of soda and chlorite of potash, mingled with chloride of sodium and chloride of potassium, and that of chlorite of lime mingled with chloride of calcium and hydrate of lime —a compound which is commonly termed chloride of lime; for these compounds are now very much employed not only as bleaching agents but as destroyers of miasma, and it is therefore of importance to know how great a quantity of chlorine they disengage upon being treated with acids. With respect to the analysis of the chloride of lime, or rather the estimation of the chlorine, GAY-LUSSAC (*Annales de Chimie et de Physique*, T. XXVI. p. 162) has given a method by which the quantity of chlorine contained in a weighed quantity of the substance can be ascertained. This method consists in pulverising a weighed quantity of the chloride of lime with a given quantity of water, and then bleaching with the mixture a given quantity of a solution of indigo in sulphuric acid previously diluted with water. The greater or smaller quantity of the bleached indigo solution indicates the quantity of the chlorine which is expelled from the chloride of lime by the sulphuric acid of the indigo solution. When this operation is not conducted with proper precaution, it is possible, according to MORIN (*Journal de Pharmacie, Oct.* 1828), to obtain very uncertain results. The diluted indigo solution is moreover affected in its composition when kept long. When the solution of indigo is mixed with the solution of chloride of lime, a slight portion of the chlorine sometimes escapes before it has exerted its bleaching action on the indigo. This is the case, when the mixture is made very slowly. The effect produced in these experiments depends indeed very much on the greater or lesser degree of rapidity with which the two liquids are mixed together. **Morin** has, on this account, recommended a different mode of examination. It is still unknown, however, whether his method affords more certain results than that which it is intended to supersede.

When the chloride of lime consists merely of chlorite of lime mingled with the portion of chloride of calcium which must necessarily be produced in its preparation, the quantity of chlorine which can be disengaged, by treating the compound with an acid, may be most accurately determined as follows: A weighed quantity of the chloride of lime is decomposed in a suitable apparatus by diluted sulphuric acid, and the disengaged chlorine gas is led into a diluted solution of ammonia. The ammoniacal solution is then supersaturated by nitric acid, and is mixed with a solution of nitrate of silver, which precipitates the chlorine in the state of chloride of silver. The apparatus employed for this purpose may be such as that described at p. 229. It is unnecessary, however, to connect so many flasks of ammonia with the gas bottle, as are represented in the figure above referred to. In order, at the end of the distillation, to drive all the chlorine from the body of the gas bottle into the ammonia, a solution of carbonate of ammonia may be made use of in the manner already described. It is only necessary to take care that an excess of sulphuric acid be then present in the gas bottle.

This method of examination cannot, however, be employed, when the chloride of lime contains chlorate of lime. The presence of chlorate of lime is very frequent when, in the preparation of the chloride of lime, the production or application of heat has not been avoided with sufficient care, or when the hydrate of lime has not been treated with an excess of chlorine.

According to **Liebig** (**Poggendorff's** Annalen, T. xv. p. 545), the solutions of the chlorites convert a solution of sulphuret of barium into sulphate of barytes; in effecting this change, the oxygen of the chlorous acid converts the sulphur into sulphuric acid, and the oxygen of the base combined with the chlorous acid converts the barium into barytes. If, therefore, the quantity of the sulphate of barytes were to be determined, which can be readily done by supersaturating the whole with a free acid, as, for example, with muriatic acid, and igniting the sulphate of barytes to free it from the precipitated sulphur, then the quantity of the chlorous acid could be calculated. Hence it is easy to discover how much chlorine is disengaged from the chloride of lime by acids; for this quantity of chlorine is equivalent to the quantity of oxygen which has been taken up by the sulphuret of barium to give origin to sulphuric acid and barytes.

Separation of Chlorides from Chlorates.—When a chloride and a chlorate are contained in the same solution, and are to be respectively quantitatively estimated, the separation can be effected without the least difficulty if no chlorite be also present in the solution. The solution, if it contain no free base, is mixed with a solution of nitrate of silver, which precipitates merely the chlorine of the chlorides, in the state of chloride of silver. From the weight of this precipitate, the quantity of the chlorine in the chloride can, therefore, be easily reckoned. If, now, another portion of the solution be evaporated to dryness, then ignited, and again dissolved in water, or in very dilute nitric acid, and mixed with a solution of nitrate of silver, it affords a precipitate of chloride of silver, which contains not only the chlorine belonging to the chloride, but that also which formed part of the chlorate. It is then merely necessary to estimate the quantity of chlorine in the chloride of silver, and to deduct the proportion of chlorine known to belong to the chloride of the compound. The remainder indicates the quantity of chlorine contained in the chlorate. It is then easy to calculate the quantity of the chloric acid contained in the solution.

XLVIII. BROMINE.

Decomposition of Bromides by Sulphuric Acid.—The quantitative estimation of bromine when combined with metals can, in most cases, be, upon the whole, best effected as follows: A weighed quantity of the compound of bromine is decomposed, with the aid of heat, by sulphuric acid.

The quantity of the metal is then calculated from the weight of the resulting sulphate of oxide, and that of the bromine from the loss sustained. As the decomposition of metallic bromides by sulphuric acid produces a disengagement of hydrobromic acid gas, sulphurous acid, and bromine, of course the decomposition must not be effected in a platinum crucible, but in a porcelain capsule. Some bromides, however, are incapable of being decomposed by sulphuric acid: the perbromide of mercury is an example.

Decomposition of Bromides by Sulphuretted Hydrogen.—There are still other methods of determining the quantity of the metal contained in a metallic bromide. When the compound is soluble in water or in dilute acids, and the base is capable of being precipitated, either from an acid solution by sulphuretted hydrogen gas, or from a neutral solution by bihydrosulphuret of ammonia, then the operator can employ one of these precipitants to separate the metal from the bromine, whereupon the metal can be quantitatively estimated.

Decomposition of Bromides by Alcaline Carbonates.—When, however, the compound dissolves neither in water nor in acids, the quantity of the base can still be often determined as follows: A weighed portion of the compound is ignited with carbonate of potash or carbonate of soda, and the ignited mass is treated with water. The resulting bromide of potassium or bromide of sodium, and the excess of carbonated alcali then dissolve, while the metal, in the state of oxide, remains undissolved, unless, indeed, the solution of carbonated alcali be capable of dissolving it.

Precipitation of Bromine by a Solution of Silver.—According to these methods, however, the quantity of the bromine is found only from the loss sustained. But it is possible to determine also the quantity of the bromine contained in compounds which are soluble in water, by direct experiment; because bromine produces insoluble precipitates, not only with silver, but with several other metals. It is probable, therefore, that a solution of nitrate of silver might be employed with as much advantage in the precipitation of bromine from bromides, as in the precipitation of chlorine from chlorides; for, the bromide of silver and the chloride of silver appear to be very similar in their relations not only towards water, but towards diluted nitric acid and ammonia. It has, however, not yet been determined by experiment, whether solutions of silver precipitate bromine from bromides with the same accuracy that they precipitate chlorine from soluble chlorides.

Separation from Chlorine.—No method of quantitatively separating bromine from chlorine has yet been discovered.

XLIX. IODINE.

Decomposition of Iodides by Sulphuric Acid.—The quantitative estimation of iodine in metallic iodides can, in most cases, be effected in the same manner as that of bromine in bromides, namely, by decomposition with sulphuric acid. As the decomposition of metallic iodides by sulphuric acid is accompanied by the disengagement of sulphurous acid and free iodine, so must here also, the employment of a platinum vessel be avoided, and a vessel of porcelain be substituted in its stead. From the quantity of the resulting sulphate of oxide, the quantity of the metal is reckoned: the quantity of the iodine can only be found from the loss sustained. Some metallic iodides, such as the periodide of mercury, are indecomposable by sulphuric acid.

Decomposition of Iodides by Sulphuretted Hydrogen.—When metallic iodides are soluble in water or in acids, it is easy to separate the iodine from the metals which are precipitable either from acid solutions by sulphuretted hydrogen gas, or from neutral solutions by bihydrosulphuret of ammonia.

Decomposition of Iodides by Alcaline Carbonates.—Metallic iodides which are insoluble in water, can also be decomposed by ignition with carbonate of potash or carbonate of soda. Upon treating the ignited mass with water, the iodide of potassium or iodide of sodium, and the excess of the carbonated alcali dissolve, while the metal, in the state of oxide, remains behind, unless, indeed, it be soluble in the solution of carbonated alcali.

Precipitation of Iodine by a Solution of Silver.—As the compounds formed by iodine with a great number of metals are insoluble in water, so the iodine could be precipitated from its compounds which are soluble in water by a great number of metallic solutions. Supposing iodine to have been thus precipitated, the quantity of the iodine is to be reckoned from the weight of the insoluble iodide. It is not known with certainty, however, what metallic solution is best adapted to this purpose. Probably the employment of a solution of nitrate of silver would be the most advantageous; the iodide of silver must then be precipitated with the same precaution that is necessary to be taken in the precipitation of chloride of silver.—It remains to be remarked, that many metallic iodides which are insoluble in pure water, possess a slight degree of solubility in solutions of other salts.

Separation from Bromine and Chlorine.—Iodine, contained in compounds which are soluble in water, can, according to the recommendation of BALARD and SOUBEIRAN (Journ. de Pharm. 1828, p. 421), be separated from the soluble compounds of bromine and chlorine, by conversion into protoiodide of copper: this substance does not dissolve in water, while the perbromide of copper and perchloride of copper produced at the same time, both, if both be present, dissolve. If an iodide which is soluble in water, for example, iodide of potassium or iodide of sodium, be dissolved and mingled with a solution of sulphate of deutoxide of copper, it produces no periodide of copper, which does not appear to exist; nothing, therefore, but protoiodide of copper is formed; on which account, half the iodine becomes free, and, dissolving in the solution, gives it a brown colour. To precipitate the whole of the iodine in the state of protoiodide of copper, it is necessary to adopt the following process of BERZELIUS (POGGENDORFF's Annalen, T. XII. p. 604): The dissolved metallic iodide is mingled with a solution containing one part of crystallised deutosulphate of copper, and 2¼ parts of protosulphate of iron, which is added until it ceases to produce a precipitate. The metal which was combined with the iodine is thereby converted into sulphate of oxide, while the protosulphate of iron is converted into persulphate of iron, at the expense of a portion of the deutosulphate of copper. The copper of the latter then combines with that portion of iodine which would remain free in the solution, if merely a solution of deutoxide of copper, without the addition of protoxide of iron, were employed to precipitate it.—The precipitated protoiodide is filtered, washed, dried, and weighed. The quantity of iodine that it contains is then calculated. The compounds of bromine and chlorine, when these were present, remain undecomposed in solution. The bromine or chlorine is precipitated from the filtered liquid by a solution of nitrate of silver.

L. NITROGEN.

Quantitative Estimation of Nitrogen Gas.—The quantitative estimation of nitrogen, as nitrogen gas, occurs only in the separation of this gas from other gases. The usual method of proceeding is to permit all the other gases which are combined with the nitrogen gas to be absorbed by different reagents, and then to measure the volume of the remaining nitrogen gas. The precautionary measures which are to be observed in this operation will be fully discussed in the following section, in which will also be explained the method of analysing mixtures of nitrogen gas with oxygen gas, such, for example, as atmospheric air.

Quantitative Estimation of Free Nitric Acid.—Of all the oxides of nitrogen, nitric acid is unquestionably the most important. Its quantitative estimation is, in many cases, attended with difficulties. When nitric acid is contained in a liquid, and is not accompanied by any other acid, its quantity can be very accurately estimated by the process which follows: A solution of hydrate of barytes (barytic water) is added to the solution in quantity sufficient to make it change the colour of red litmus paper to blue. The excess of barytes is then usually removed, by leading a current of carbonic acid gas through the solution. This precipitates the excess of barytes, in the state of carbonate of barytes. A small portion of the carbonate of barytes remains dissolved, however, in the excess of carbonic acid. It is, therefore, necessary to warm the solution, after the gas has been passed into it. The precipitated carbonate of barytes is separated by filtration. The filtered solution then contains nothing but the nitrate of barytes. It is cautiously evaporated by a gentle heat to dryness, and the dry salt is weighed. The quantity of the nitric acid is then calculated.—It is better, however, to operate as follows: To the solution which contains the nitric acid, a sufficient quantity of hydrate of barytes is added, and the whole is then slowly evaporated to dryness. The precipitation of the excess of barytes by carbonic acid gas is omitted as unnecessary, since the barytes acquires a sufficient quantity of carbonic acid from the atmosphere, while the evaporation is going on, to become wholly converted into carbonate of barytes. The mass which has been evaporated to dryness is treated with water, and the undissolved carbonate of barytes is filtered. The solution of the nitrate of barytes filtered from the carbonate of barytes can be now evaporated to dryness, and the quantity of the nitric acid can be calculated from the weight of the dry residue. But it is far better to precipitate the barytes from the solution of nitrate of barytes by the addition of diluted sulphuric acid. The operator then calculates the quantity of the nitrate of barytes from the weight of the precipitated sulphate of barytes. This it is very easy to do, because the quantity of the precipitated sulphate of barytes is to the quantity of the nitrate of barytes, as the atomic weight of the former to that of the latter. From the weight of the nitrate of barytes, the operator then reckons the quantity of the nitric acid.

Separation of Nitric Acid from Bases by Sulphuric Acid. When nitric acid is combined with bases, the nitrates are decomposed in a platinum crucible by sulphuric acid; and the nitric acid and excess of sulphuric acid are expelled by exposure to a feeble red heat. From the weight of the resulting sulphates, the operator calculates the quantity of the bases. The quantity of nitric acid is ascertained from the loss. It will be understood, that this method cannot be employed when the sulphates produced are decomposable by mere ignition.

Separation of Nitric Acid from Bases by Heat.—When the nitrates are exposed to a red heat, they leave, in most cases, nothing but the pure metallic oxide. The quantity of the nitric acid can then be determined by the loss of weight, provided no water of crystallisation was contained in the salt. The compounds of nitric acid with the metallic oxides, properly so called, do not require so strong a heat for their conversion into oxides as the compounds of nitric acid with the alcalies and alcaline earths. The latter can only be completely decomposed by exposure to an extremely powerful heat, and then they attract carbonic acid from the atmosphere, unless protected from its action.

Separation of Nitric Acid from Bases by Sulphuretted Hydrogen Gas.—The bases can be separated from nitric acid by another process, which admits also, in many cases, of the direct estimation of the acid. Suppose the nitrate to be soluble in water, and the base to contain a metal which can be precipitated from solution by sulphuretted hydrogen gas. The base is then precipitated by this reagent. The solution filtered from the metallic sulphuret contains the whole of the nitric acid and a small quantity of sulphuretted hydrogen. It is mixed with a solution of hydrate of barytes in excess, and is subsequently treated in the manner which has been described above. When the whole is evaporated to dryness, the excess of barytes becomes saturated with carbonic acid, while the small quantity of sulphuret of barium, produced by the excess of sulphuretted hydrogen, is converted by oxidation, first into hyposulphite, and finally into sulphate of barytes. When, now, the dry mass is treated with water, the only thing which dissolves is nitrate of barytes. The solution is filtered, and treated with sulphuric acid. The weight of the precipitated sulphate of barytes affords data for calculating the quantity of the nitric acid.

Decomposition of insoluble Basic Nitrates.—When nitric acid is combined with a metallic oxide which can be completely precipitated from its solution by sulphuretted hydrogen gas, but happens to form, with that oxide, a compound which is insoluble in water, the analysis may be performed in the manner to be now described. Many basic nitrates require this mode of treatment, in consequence of their insolubility. The compound is mingled with water, and a current of sulphuretted hydrogen gas is passed through the mixture until the gas ceases to be absorbed. It is best to make the mixture in a flask which can be closed with a glass stopple. When the sulphuretted hydrogen gas has been led into the mixture for some time, the flask is separated from the glass bottle. If the liquid then smells very strongly of sulphuretted hydrogen, the flask is closed with the stopple and well shaken. By this means, that portion of the compound is decomposed which had previously escaped the action of the gas. If, upon reopening the flask, the liquid still smells strongly of sulphuretted hydrogen; it proves that the decomposition is fully effected. If this is not the case, the passing of the sulphuretted hydrogen gas into the liquid must be continued.—The solution filtered from the metallic sulphuret is treated in the same way as the solution obtained in a similar manner, in the decomposition of the soluble nitrates. This mode of treatment has been described above.

The nitrates which are insoluble in water can be analysed equally well by a process first described by MITSCHERLICH, j. (POGGENDORFF'S Annalen, T. IX. p. 403), and which is as follows: A weighed quantity of the compound for examination is treated with a solution of sulphuret of barium, and being poured into a flask which can be closed, is allowed to digest with it for a considerable time. The resulting metallic sulphuret is then brought upon a filter, and the filtered solution, which contains nitrate of barytes and the excess of sulphuret of barium, is exposed to a current of carbonic acid gas. By this means, the sulphuret of barium is converted, under disengagement of sulphuretted hydrogen gas, into carbonate of barytes. This decomposition is effected very slowly, however, and often requires that the current of carbonic acid gas be kept up for more than twenty-four hours. It is advisable to evaporate the whole to dryness, and to treat the dry residue with water. Thereupon, the nitrate of barytes alone dissolves and is separated from the other matters by filtration. The solution is then analysed by the process described above.

In this method, as well as in the preceding, it is essential that the insoluble nitrate submitted to experiment be reduced to an extremely fine powder; since a portion of it can otherwise easily escape the action of the sulphuretted hydrogen gas or the sulphuret of barium.

Separation of Nitric Acid from Manganese, Zinc, Iron, and Cobalt.—When the nitrate to be examined contains a metallic oxide which is capable of being accurately precipitated in the state of metallic sulphuret, but the precipitation of which is incapable of being effected in a neutral solution by sulphuretted hydrogen gas, and requires the employment of the soluble sulphurets of alcaline metals, as, for example, is the case with the oxides of manganese, iron, zinc, and cobalt, then the solution of the nitrate, or if it be insoluble, a weighed quantity of the salt finely pulverised, is treated with a solution of sulphuret of barium, in the manner which has been described above.

Separation of Nitric Acid from Metallic Oxides by Barytes.—When the nitrate to be examined is soluble in water, and contains a base that can be fully precipitated from its solution, by the hydrate of barytes, which is the case with most of the oxides of metals, then the method of proceeding, to ascertain the quantity of the nitric acid, is more simple. A weighed quantity of the salt is digested with an excess of a solution of hydrate of barytes, and towards the end, the mixture is made to boil. The whole is then cautiously evaporated to dryness, and the dry mass is treated with water. Nitrate of barytes alone dissolves, while carbonate of barytes and the base which was precipitated by the hydrate of barytes remain undissolved.

Separation from Barytes and Strontian.—When the nitrate of barytes or strontian is to be analysed, the solution is first mingled with sulphuric acid, and the quantity of the base is calculated from the weight of the resulting sulphate of barytes or strontian. The solution is filtered and the excess of sulphuric acid is separated by barytes-water. After which, the nitric acid is estimated by the process repeatedly described.

Separation from Alcalies.—By following, in the analysis of the nitrates, the methods which have been described thus far, it is possible, in most cases, to estimate not only the quantity of the base, but also of the nitric acid. If any of the salts contain water of crystallization, the quantity is ascertained from the loss experienced.—But there are some nitrates, in the analysis of which, the quantity of nitric acid cannot be directly determined by experiment, but can only be estimated from the loss. This is the case, for example, with the compounds formed by nitric acid with the alcalies. Such nitrates as these must be decomposed by sulphuric acid. The quantity of the alcali is learned from the weight of the sulphate of alcali. The quantity of the nitric acid is then indicated by the loss.

Estimation of Nitric Acid in Mineral Waters which contain Alcaline Nitrates.—When, however, nitrates with alcaline bases are contained in a solution, and the operator is desirous of accurately determining the quantity of nitric acid, he may proceed as follows: The solution is mixed, in a retort, with sulphuric acid, and the whole is distilled by a moderate heat to dryness. The distilled liquor is collected in a receiver containing barytes-water. Care must be taken during the distillation, that none of the volatilized acid escapes. The liquor in the receiver is afterwards slowly evaporated to dryness, and the dry mass is treated with water. The nitrate of barytes is thereupon dissolved, while the carbonate of barytes remains behind. If any sulphuric acid has been driven over from the retort during the distillation, the carbonate of barytes will be accompanied by sulphate of barytes. The quantity of the nitric acid contained in the solution of nitrate of barytes is learned by precipitating the barytes by sulphuric acid, as described above.—This method can be employed with much advantage, in the quantitative estimation of the nitric acid in the mineral waters which contain nitrates.

Analysis of the Nitrites[*].—The best way to analyse the compounds of nitrous acid is to estimate the quantity of the base, and to reckon the acid from the loss experienced. The nitrites can be decomposed by sulphuric acid and the quantity of the nitrous acid determined from the weight of the sulphate produced. The nitrites can also be decomposed by ignition, in which case the base alone remains behind. It is difficult, however, by these methods, to estimate the quantity of the water of crystallisation in the compound.

Analysis of the Oxides of Nitrogen by Ignition with Metals.—All the oxides of nitrogen can be completely decomposed, by being passed in vapour over red-hot copper or iron. This method was first employed by DULONG (*Annales de Chimie et de Physique*, T. II. p. 319) in his researches respecting the water-free nitrous acid. He made use of a tube of porcelain, in which he placed a weighed quantity of well-cleaned copper or iron wire, in great excess. Both ends of the tube were furnished with corks having glass tubes passed through them. One of these glass tubes served to lead the gas into the porcelain tube; the other to convey it thence, after decomposition, to be measured. The gas issuing from the porcelain tube was always passed through a glass tube filled with chloride of calcium, for the purpose of freeing it completely from every trace of moisture. The portion of the porcelain tube, where the metal wire lay, was made red-hot, and the gas was then passed through it.—By the decomposition which ensues, oxide of iron, or oxide of copper is formed, and nitrogen gas is liberated. After the experiment is ended, the weight of the resulting oxide of iron or oxide of copper is ascertained by weighing the metallic wire. The quantity of the nitrogen is learned by measuring the volume of the nitrogen gas. If the compound thus analysed contained water, the water is partly absorbed by the chloride of calcium, and when iron wire has been employed, is partly decomposed. In the latter case, the nitrogen gas is mingled with hydrogen gas.

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[*] The nitrites of Berzelius, are the compounds which, in this country, are usually termed hyponitrites.—TRANSLATOR.

Separation of Nitrogen Gas from other Gases.—Mixtures of nitrogen gas with other gases are analysed in another manner. It will be better, however, to treat of this subject in the following section, in connexion with gaseous analysis in general. The method of examining mixtures of nitrogen gas and oxygen gas, such as atmospheric air, shall be spoken of at the same time.

Separation of Nitrogen from Chlorine and Iodine.—The compounds of nitrogen with chlorine and iodine are so easily decomposable, that it is difficult to analyse them with accuracy, and impossible to experiment upon them without danger. As they become decomposed into their elements by exposure to a high temperature, it might indeed be possible to determine the respective proportions of their constituents by separating them in this manner; but, unfortunately, the products cannot be very accurately collected, since the decomposition is attended by a violent explosion.—If these compounds be brought into contact with copper and water, decomposition ensues, and the products are compounds of copper with chlorine or iodine, and free nitrogen gas. The quantity of chlorine or iodine can then be determined with accuracy; and the free nitrogen gas can be collected and measured.

Separation of Nitrogen from Carbon: Analysis of Cyanurets.—The compounds formed by carbon and nitrogen, that is to say, by cyanogen, with other substances, are of great importance. The analysis of the cyanurets can be performed by determining with accuracy the quantity of the metal, and calculating the cyanogen from the loss. Most of these compounds can be converted into chlorides by muriatic acid. The decomposition is accompanied by the disengagement of hydrocyanic acid. If the weight of the resulting chloride is determined, the composition of the cyanuret can be readily calculated. But then it must contain no water of crystallisation.—If the cyanogen is combined with metals which can be completely precipitated from solution, as sulphurets, by sulphuretted hydrogen gas, the decomposition may be effected by means of this gas, even when the cyanurets are insoluble in water. It is only necessary to mingle them with water and to pass a current of sulphuretted hydrogen gas through the mixture. The metal is thereby converted into metallic sulphuret, which can be weighed. The liquid filtered from the metallic sulphuret then contains hydrocyanic acid.

Analysis of Cyanogen.—When, however, the operator is desirous of determining the quantity of the cyanogen by a direct experiment, he may proceed as follows: A weighed portion of the cyanuret is mingled with a suitable quantity of deutoxide of copper, and is then ignited. The cyanogen is converted into carbonic acid gas and nitrogen gas, in the proportion of two volumes of the former to one volume of the latter. It is easy to ascertain, from the bulk of the gaseous mixture, the quantity of the cyanogen which was contained in the cyanuret. All the precautions which are to be taken in the performance of this experiment, with a view to insure accuracy in the results, will be circumstantially treated of in the following section; so that the description may be passed over in this place.

Decomposition of double Cyanurets by Sulphuric Acid.—The double cyanurets are prepared more generally than the simple cyanurets, and the compound of cyanogen with iron and other cyanurets, more frequently than any other. The analysis of these compounds is more difficult than the analysis of the simple cyanurets; because they are much less easy of decomposition. If they contain metals which, when contained in other compounds, can be completely precipitated from solution by sulphuretted hydrogen gas, yet, in most cases, no decomposition can now be effected by sulphuretted hydrogen gas. And even the double cyanurets, which contain percyanuret or protocyanuret of iron, give no precipitate of sulphuret of iron, upon being treated with bihydrosulphuret of ammonia, not even when these compounds are soluble in water. It is the same with other substances. Metals which can be completely precipitated from other solutions by certain reagents, afford no precipitate with the same reagents, when they are combined with cyanogen. If treated with sulphuric acid, and that, too, in a concentrated state, the compounds alluded to are only completely decomposed when the mixture has been so long and so powerfully heated as to expel the excess of sulphuric acid. At a lower temperature these compounds dissolve in concentrated sulphuric acid, without undergoing decomposition. When the decomposition has been effected by heated sulphuric acid, the constitution of the cyanuret can be calculated from the weight of the resulting sulphate.

Decomposition of double Cyanurets by Nitric Acid.—The decomposition of these double cyanurets can also be effected in a great number of cases by the process which follows: A weighed quantity of the compound, in a pulverised state, is placed in a matrass and treated with fuming nitric acid. When the action of the acid is over, the matrass is exposed to a continued heat, and muriatic acid is added. The metals which were combined with the cyanogen are thus converted into oxides. The weight of the latter is then determined, after which, it is easy to calculate the quantity of the cyanogen, provided the compound contained no water of crystallisation.

Decomposition of double Cyanurets by Peroxide of Mercury.—The decomposition of these compounds can often be effected by peroxide of mercury. If the solution of such a compound, or when it is insoluble, if the powder mingled with water, be boiled with an excess of peroxide of mercury, then the metals combined with the cyanogen become oxidised, while the reduced mercury combines with the cyanogen to form cyanuret of mercury, which dissolves. When protocyanuret or percyanuret of iron is contained in the compound submitted to examination, the iron is converted into peroxide and precipitated; but its precipitation is only completely effected by a long digestion. The solution is filtered and the precipitate is ignited. The excess of peroxide of mercury then volatilizes, and the peroxide of iron alone remains behind. This method of decomposition appears, however, to be one of those which are little deserving of recommendation, since the peroxide of mercury is incapable of effecting a complete decomposition. If the cyanuret contains cyanuret of potassium, then, according to C. GMELIN (SCHWEIGGER'S Jahrbuch, T, XXXIV. p. 331), the precipitated peroxide of iron is contaminated by potash, which cannot be separated by washing the precipitate.

Decomposition of double Cyanurets by Heat.—The double cyanurets can also be decomposed by being ignited in the open air. But it requires a very long-continued red heat to effect the decomposition, particularly when the compound contains cyanuret of potassium or cyanuret of sodium. The metals of the cyanurets are thus converted into oxides, which are afterwards separated.

Estimation of the Quantity of Cyanogen in the double Cyanurets.—If the operator wishes to determine the quantity of cyanogen in the double cyanuret by a direct experiment, he may proceed as with the simple cyanurets. A weighed portion of the compound is ignited with deutoxide of copper, and the quantity of the cyanogen is determined by estimating the bulk of the gaseous mixture of two volumes of carbonic acid gas with one volume of nitrogen gas which is produced by the decomposition. If any water is produced in the experiment, it will have been contained in the compound either as hygrometric water or as water of crystallisation.

Separation of Cyanurets from Water of Crystallisation.—The quantity of the water of crystallisation contained in these compounds can, in a great number of cases, be very easily estimated. It is only necessary to heat them gently and to weigh them: the loss experienced gives the quantity of water. The compounds of protocyanuret of iron with cyanuret of potassium and cyanuret of sodium lose their water of crystallisation completely, if placed for some time either in a warm situation, or near a quantity of sulphuric acid under the receiver of an air-pump. On the contrary, however, the compounds of protocyanuret of iron with cyanuret of barium and cyanuret of calcium, retain a small portion of their water with much obstinacy. This can then be estimated only by decomposing the compound with deutoxide of copper.

Analysis of Cyanous and Cyanic Acids, and of the Cyanites and Cyanates.—With respect to the compounds of cyanogen with oxygen, and those formed by the combination of cyanous and cyanic acids with bases, their analysis is most accurately effected by determining experimentally the quantity of the base. If the operator wishes to determine in the same manner the quantity of the cyanogen contained in the acids, then a weighed quantity of the salt in which the quantity of the base, and consequently that of the acid, has already been determined, is ignited with deutoxide of copper. The decomposition affords a gaseous mixture of two volumes of carbonic acid gas with one volume of nitrogen gas. The quantity of the cyanogen is readily determined from the bulk of this mixture. To determine the quantity of the bases in the cyanites, there are, according to **Wöhler** (**Poggendorff's** Annalen, T. I. p. 117), a variety of methods of proceeding. A weighed quantity of the salt is exposed to the action of a current of dry chlorine gas, the salt being in the mean time heated by a spirit lamp. The apparatus required for this experiment is such as that represented at page 83. The decomposition affords a large quantity of carbonic acid gas and of muriate of ammonia; which, if the tube be too narrow, can occasion a stoppage. The muriate of ammonia must therefore be continually expelled from the tube by the application of heat. When the apparatus is cold, the resulting metallic chloride is weighed, and the quantity of the metallic base is calculated.

As the cyanous acid existing in compounds which are soluble in water, readily decomposes into ammonia and carbonic acid, in consequence of which the bases become converted into carbonates, it is possible, according to **Wöhler**, to derive benefit from this property, in the analysis of such cyanites. The salt is moistened in a platinum crucible, and is afterwards gently dried and ignited. This operation is repeated. Ammonia is disengaged, and the substance remaining is the base of the cyanite in combination with carbonic acid, providing that the carbonic acid has not been driven away by the ignition.

The cyanites, whether dissolved in water or insoluble in water, can also be decomposed by muriatic acid. The mixture of cyanite and muriatic acid is evaporated to dryness, and the residue is ignited. The weight of the resulting metallic chloride indicates the composition of the cyanite.

—The bases which may be combined with cyanous acid can, besides, be separated from their solutions in water, according to the methods described in the preceding sections. The cyanites which are insoluble in water require only to be dissolved by an acid, to permit of the quantitative estimation of the bases by the usual processes.

LI. HYDROGEN.

Quantitative Estimation of Hydrogen Gas.—When hydrogen, in the state of gas, is mixed with other gases, as, for example, with oxygen gas, the operator determines the volume, and thereby the quantity, of the hydrogen gas, from the diminution of bulk which takes place, when the gaseous mixture of hydrogen and oxygen is inflamed. The diminution of bulk, if oxygen gas remain behind, indicates the volume of the hydrogen gas; it is two-thirds of the volume of gas which has disappeared.

Description and Use of the Eudiometer.—The analyst employs, in this experiment, an instrument of which a representation is given below. It consists of a glass tube *a*, which must be of thick glass, closed at one end, and open at the other. Near the closed end, two wires of iron or platinum, *b* and *c*, pass through the glass. They must be cemented into the tube air-tight, or fused in with two thin glass tubes, and they must be so situated within the tube, that their points may stand opposite to one another at the distance of one or more lines, but the points must not come into contact. The ends of the two wires outside the tube may be rounded off. The space within the tube is now to be divided into equal parts. In experiments performed merely to find the relative proportions of mixed gases, the divisions can be arbitrary; in other cases, particularly when the weight of the substance is to be reckoned from the measured volume of the gas, the operator employs as a measure of unity, the bulk of a *cubic centimeter*. The method of producing an accurate division of the tube, is as follows: The operator closes a small glass tube at one end, and then fills it with as much mercury as occupies the bulk of a *cubic centimeter;* this bulk is equal to that of a gramme of water at the temperature of 39·2° Fahr.*. To fill the same space with mercury, so many grammes of that metal must be taken as the specific gravity of the mercury employed is greater then the specific gravity of water. The upper part of the little glass tube is then cut off quite close to the surface of the mercury, and the edges of the tube are ground away more or less, according as it may be requisite. In this manner it is brought to pass, that when the little tube is filled with mercury, and the excess of mercury is removed by a little plate of ground glass, then the little tube contains exactly as much mercury as is equal in bulk to a cubic centimeter. This cubic centimeter of mercury is now poured into the glass tube, which is to be graduated; the glass tube is placed in a position perfectly perpendicular, and the point to which the mercury reaches is marked on the outside of the glass tube by means of a writing diamond. The operation is repeated in the same manner, until the graduation of the glass tube is completed.

The process of analysing the gaseous mixture is as follows: The glass tube is filled with mercury, care being taken, in filling it, to expel the little bubbles of atmospheric air which are apt to adhere to the sides of the tube. To effect this, the operator fills the tube at first not quite full of mercury; he then shakes the mercury up and down the tube; and finally, rubs the interior sides of the tube with the plume of a feather. The tube being then completely filled with mercury, is placed in a trough of mercury, and a small quantity of the gaseous mixture which is to be examined, is passed into the tube. Thereupon, the glass tube *a* is placed in a larger glass *e*, which must be filled with mercury, and be at least as tall as the glass tube *a*. To be able to transfer the tube *a* from the trough to the glass *e*, the tube is placed, while in the trough, in a small porcelain crucible, and is removed in this, into the glass *e*. The operator then presses down the tube *a*, until the mercury within and without the tube is on a level, upon which the volume of the gaseous mixture can be determined with accuracy. That the tube may be held steadily in the mercury, it is pinched between the cheeks of a holdfast, which can be screwed higher or lower on an upright wooden support, as shown in the subjoined figure.

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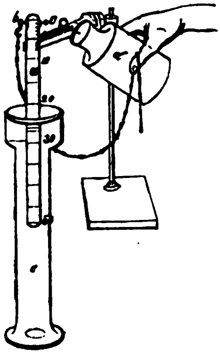
* In England, the *cubic inch* is generally employed as the measure of unity. A cubic inch is equivalent to 16·386176 cubic centimeters. A cubic inch of water at the temperature of 62° Fahr. and 30 inches of barom. pressure, weighs 252·458 troy grains. A cubic inch of mercury at the same temperature, weighs 3425·35 grains. The hundredth part of a cubic inch of mercury weighs 34·25 grains nearly. The gramme is equal to 15·438 troy grains.—TRANSLATOR.



The gaseous mixture of hydrogen and oxygen is thereupon inflamed by an electric spark. The best way to give this spark, is to wind one end of a metallic chain or wire about the wire *b*, and the other end of the chain or wire about the outer coating of a charged Leyden jar *d*; things being thus prepared, the knob of the jar is brought into contact with the wire *c*, upon which an electric spark springs through the gaseous mixture, from *c* to *b*, and the gas is inflamed.

If the gaseous mixture consisted of two volumes of hydrogen gas with more than a volume of oxygen gas, then, after the detonation, there remains behind precisely so much of the oxygen gas as existed in the mixture in excess above the quantity which was requisite to combine with the hydrogen, namely, one half the volume of the hydrogen gas. The glass tube *a* is then sunk into the mercury, until the mercury which is within the tube is on a level with that on the outside: the volume of the residual oxygen gas is then measured. As the gas which is made to disappear by the detonation, consists of two volumes of hydrogen gas to one volume of oxygen gas, it is easy to find the relative proportions of the mixed gases.

If the gaseous mixture consisted of two volumes of hydrogen gas and less than one volume of oxygen gas, then the gas which remains is hydrogen gas. The operator measures the volume of the remaining hydrogen gas, and calculates from the quantity of gas which has disappeared, the relative proportions of oxygen and hydrogen.

When, however, it is not known whether the gas which remains after the detonation, be oxygen gas or hydrogen gas, then, after determining the volume of the remaining gas, an additional portion of oxygen gas is introduced. This oxygen gas must not be in less quantity than half the volume of the gas to which it is added. An electric spark is again passed through the gaseous mixture. If it produce no diminution of bulk, then the gas which remained after the first explosion was oxygen; if, on the contrary, it produce a diminution of bulk, then the gas which formerly remained was hydrogen.

Preparation of pure Oxygen Gas.—The requisite quantity of oxygen gas is prepared as follows: A small quantity of chlorate of potash is placed in a small glass bulb, blown on the end of a glass tube, and the upper part of the glass tube is then drawn out to a fine point; the part or neck so drawn out is bent, at the same time, in such a manner, that the whole apparatus assumes the form of a little retort. The chlorate of potash is then melted by the flame of a small spirit lamp, and when it is perceived, from the rapid disengagement of gas, that oxygen gas is set free, then the point of the glass tube is melted and sealed up. The little retort is then allowed to cool.—Whenever the analyst desires to add a little pure oxygen gas to another gas, he breaks off the end of the little retort, brings the chlorate of potash into fusion, and passes the end of the little retort into the mercury; the disengaged oxygen gas then rises into the glass tube.

It remains still to be remarked, that a gaseous mixture of oxygen and hydrogen is not inflamed by the electric spark, when the volume of one of the gases is in too large a proportion in relation to the other. If, for example, the gaseous mixture contains, according to DAVY (GILBERT'S Annalen, T. LV. p. 101), 14 volumes of oxygen gas, or, according to HUMBOLDT and GAY-LUSSAC (GILBERT'S Annalen, T. XX. p. 52), only 9½ volumes of oxygen gas to 1 volume of hydrogen gas, or if, on the contrary, it contains, according to **Davy**, 26 volumes of hydrogen gas to 1 volume of oxygen gas, then the electric spark occasions no detonation. By what methods the analysis is to be conducted in such cases, will be described farther on.

As the gaseous mixture of oxygen and hydrogen expands at the moment of inflammation to a very extraordinary extent, it is necessary that the volume of the gaseous mixture to be examined, should occupy but the third part of the capacity of the eudiometer in which the detonation is to take place. If the volume of the gaseous mixture submitted to analysis were permitted to be larger, the operator would run the risk of having a portion of gas forced out of the tube at the moment of inflammation, in consequence of the great expansion produced; and the experiment would, of course, in that case, be altogether inaccurate.

Mitscherlich's Eudiometer.—Since, however, it is desirable, in accurate inquiries, not to work with too trifling quantities of gas, the operator may employ in these experiments a different sort of eudiometer, which has been recommended by **Mitscherlich**. It is distinguished from the common detonating eudiometer, by having two holes bored in the glass tube, opposite to one another, and near the open end of the tube. These holes are made sufficiently large to allow of the insertion of a cork, which cork must, at the same time, close the tube air-tight. The glass tube may be filled nearly to this cork with the gaseous mixture, and yet no fear of the bursting of the tube need be entertained, on the passing through of the electric spark.

Use of Platinum in the Analysis of Gaseous Oxygen and Hydrogen.—In experiments of this description, the combination of the gases can not only be induced by the electric spark, but also, according to **Döbereiner**, by finely-divided platinum: when this substance is introduced into a mixture of oxygen gas and hydrogen gas over mercury, the combination of the two gases to water, is effected in the same manner as if an electric spark had been passed through the mixture. One part of spongy platinum is mixed with four parts of clay, and formed into a ball, to which a platinum wire is fastened. The platinum wire is bound to a fine ignited iron wire, and the ball is gently ignited, and then passed through the mercury into the gaseous mixture. The combination of the oxygen gas and hydrogen gas now gradually proceeds of itself, that is to say, if the proper quantity of clay has been added. When the diminution of the bulk of the remaining gas ceases to take place, the ball is withdrawn from the tube by means of the iron wire, and the volume of the remaining gas is determined. The operation is, in other respects, conducted like those which have been described above.—The employment of spongy platinum has the great advantage that it renders it unnecessary, in the analysis of gaseous mixtures, to use eudiometers with wires of metal cemented or fused into them. This process, however, does not give such accurate results as the detonation of the gaseous mixture by the electric spark. In accurate inquiries, therefore, the spongy platinum must not be employed. But, in those cases in which one of the gases which constitute the gaseous mixture to be examined, is in so large a proportion, in relation to the other gas, that no inflammation can be produced by the electric spark, then this method of analysis by means of the platinum ball, may be employed with great advantage: the ball must, in such a case, be made with more platinum and less clay. According to TURNER (POGGENDORFF's Annalen, T. II. p. 210), a combination of the gases can be effected in this manner, even when the proportion of one gas to that of the other, is as 1 to 100; it is then necessary, however, to employ tubes of large diameter, for in small tubes the experiment goes forward very slowly.

Precautions to be taken in all cases of Gaseous Analysis.—In these experiments, as, generally speaking, in all those which concern the quantitative analysis of gases, a particular degree of attention must be bestowed upon three circumstances, which, in the quantitative analysis of solid bodies, have no occasion to be attended to; and this attention requires to be paid to these circumstances in the most particular manner, when the gases operated upon are in large quantities. If no attention be paid to these circumstances, the results afforded by the experiments can often be extremely faulty.

Correction of Gaseous Volumes for Temperature.—The first of these three circumstances is the observation of the temperature at which the experiment is performed. When the volume of a gas is to be measured, the gas must have the same temperature as the circumjacent air. When a mixture of oxygen gas and hydrogen gas has been exploded, and the remaining gas has to be measured, the operator must wait for some time, to allow the gas and tube to cool properly. But if, from the instant at which the volume of the gaseous mixture employed in the experiment was first measured, to the instant at which the volume of the remaining gases is estimated, any change of temperature has taken place in the chamber, then a correction requires to be made on the last measurement, to provide against erroneous results. This correction requires to be made in all the cases of gaseous analysis which will be spoken of hereafter. Whenever a volume of any gas measured at a certain temperature, is to be compared with another volume measured and weighed at a totally different temperature, with a view to ascertain the weight of the first volume, this correction must invariably be attended to. Since all gases expand when heated, at the rate of 0·00375 of the volume which they occupy at 0°, for every degree of the centigrade thermometer*, it is necessary to calculate, in the first place, what would be the volume of the measured gas at the temperature of 0°. It is then easy to find how much must have been added to this volume when the gas has been measured at any temperature above 0°. Suppose, for example, that 100 volumes of gas have been measured at the temperature of + 10° centigrade, and that it is to be ascertained by calculation how many volumes this quantity of gas would occupy at + 20° cent. If the 100 volumes had been measured by 0°, and the temperature had afterwards been raised to + 10°, the gas would have been increased 10 × 0·00375 or 0·0375 of its volume, and would then occupy 103·75 volumes. If the temperature had been increased to + 20°, then it would have been increased 20 × 0·00375 or 0·075 of its volume, and would then occupy 107·5 volumes. Consequently, 100 volumes measured at the temperature of + 10° relate to the same gas measured at the temperature of + 20°, as 103·75 : 107·5. Therefore, the 100 volumes measured at + 10° occupy 103·61 volumes at + 20°.

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* The increase in volume for every degree of heat, according to Fahrenheit's scale, is $\frac{1}{480}$ part of the volume at 32° Fahrenheit.—TRANSLATOR.

Corrections of Gaseous Volumes for Pressure.—The observation of the height of the barometer is the second circumstance which requires attention in accurate experiments with gases. The determination of the changes experienced by the volume of a gas in consequence of variations in the height of the barometer, is extremely simple. The volume of the gas is inversely as the height of the barometer. The volumes of a gas measured at 0·760 and 0·750 meter, barometer height, have the same relation to one another as 0·750 : 0·760. If, therefore, the volume of a gas measured at 0·760 meter, barometer height, is 100, it must, at 0·750 meter, barometer height, become 101·3.—Although the changes which take place in the height of the barometer, even when the experiments last several days, are often very inconsiderable, and can be altogether neglected, yet the correction for barometric pressure becomes exceedingly important, when the volume of gas is measured, as is very frequently the case, at a pressure inferior to that of the atmosphere, indicated by the barometer. If, for example, a gaseous mixture has been measured over mercury in a graduated tube, at mean atmospheric pressure, and when the surface of the mercury both within and without the tube was at a level, and if, subsequently, the greater part of the gas has been made to disappear either by combustion or absorption, and the remainder is to be measured, then the following circumstance requires to be particularly attended to. If the mercurial trough is so shallow that the glass tube cannot be pressed down far enough to bring the mercury within and without the tube to the same level, the residual gas will be in an expanded state, in consequence of the pressure removed by the column of mercury which rises in the tube. In this case, the operator measures with accuracy the distance between the surface of the mercury within and without the tube, and subtracts the sum from the barometer height at which the gas was formerly measured. He has then the true pressure of the remaining gas. The reckoning is now exactly the same as before. If the whole gaseous volume was measured at 0·760 meter barometric pressure, and the distance subsequently measured between the height of the mercury within and without the tube was 0·300 meter, then the residual gas experiences a pressure of only 0·460 meter.

Correction of Gaseous Volumes for Aqueous Vapour.—The third circumstance which needs to be taken into consideration is the aqueous vapour with which gases are often saturated. If a gaseous mixture of oxygen and hydrogen intended to be analysed, be perfectly dry, yet, after explosion by the electric spark, the residual gas is rendered perfectly moist by the water produced in the operation. The same thing occurs with other gaseous mixtures when a portion of the gas has been absorbed by some solution. When, therefore, the residual gaseous volume has been measured in the usual manner, by pressing the glass tube or cylinder into the mercury until the latter is at the same height both within and without the tube, it is still necessary to deduct from this volume that of the aqueous vapour which, at the given temperature, is capable of existing in it. The quantity of the aqueous vapour, when the gas is saturated with moisture, can be easily calculated from the Tables contained in the Elementary works on Chemistry and Physics (BERZELIUS, Lehrbuch, T. I. p. 378): The operator there learns how high a column of mercury the aqueous vapour can counterpoise at each degree of the thermometer. If, for example, the moist gas measures 100 volumes, under a barometric pressure of 0·760 meter, and at a temperature of + 10° cent., it is then capable of containing a quantity of aqueous vapour which counterpoises a column of mercury of the height of 9·5 millimeters. Consequently, if the operator wishes to know how many volumes the above-named quantity of gas would occupy, in a dry state, at the given barometric pressure, he must deduct from the height of the barometer, the above 9·5 millimeters. Therefore, as 0·760 meter relates to 0·7505 meter, as 100 volumes of the moist gas relates to the dry gas; so the volume of the dry gas must amount to 98·7.—When a portion of the gas has been absorbed by a liquid, the pressure of the liquid which remains over the mercury must also be taken into account. It is better, however, to absorb the liquid by bibulous paper.

There is still another circumstance to be alluded to, which was first pointed out by FARADAY (POGGENDORFF's Annalen, T. VIII. p. 124). Dry gases when preserved over mercury, become, after a considerable length of time, totally replaced by atmospheric air. The probable cause of this is, that the contact between the glass and the mercury is not quite perfect, but that an interchange of the gas with atmospheric air takes place through the small canals formed between the vessel and the liquid. A complete exchange, however, requires more than twelve months. —It is proper, however, not to delay the analysis of gases which are confined over mercury, lest an exchange of this sort should be experienced.

Separation of Hydrogen Gas from Nitrogen Gas.—The analysis of gaseous mixtures of oxygen gas and nitrogen gas, or of hydrogen gas and nitrogen gas, is performed in the same way as the analysis described above. It was, therefore, unnecessary to introduce the description of the process at an earlier period. If the gaseous mixture consists of hydrogen and nitrogen, the operator measures the volume, and adds about half as much oxygen gas. He then again measures the volume of the gaseous mixture, and afterwards passes through it the electrical spark. The diminution of bulk which ensues, indicates the quantity of the hydrogen gas, which amounts to two-thirds of the volume that disappears. If the whole of the gas submitted to examination were to consist of hydrogen, the above-named proportion of oxygen gas would be sufficient to convert the hydrogen entirely into water. The gas which remains after the explosion, consists, therefore, of nitrogen gas and excess of oxygen gas. The volume of the nitrogen gas is ascertained by deducting the volume of the hydrogen gas from that of the mixture employed for analysis.

Separation of Oxygen Gas from Nitrogen Gas: Analysis of Atmospheric Air.—If a gaseous mixture consist of oxygen and nitrogen, if, for example, it be atmospheric air, the method of proceeding is exactly the same, except that, instead of oxygen gas, it is necessary to add hydrogen gas. It is somewhat less easy to prepare small quantities of hydrogen gas than small quantities of oxygen gas. When it is unnecessary to have the hydrogen gas quite free from aqueous vapour, it may be prepared in a gas bottle from zinc and diluted sulphuric acid. The gas bottle, in which the zinc with a little water is placed, must be closed air-tight with a cork having two holes pierced in it. One of these holes is to receive a funnel with a neck sufficiently long to reach nearly to the bottom of the bottle. The other hole is to receive a tube for leading away the gas. It is proper to employ a small flask or gas bottle. After pouring sulphuric acid into the funnel, the operator must wait until the disengaged hydrogen gas has expelled all the atmospheric air from the flask, so that when the hydrogen gas is inflamed at the mouth of the conducting tube, it burns quite steadily. The disengagement of gas must be effected very slowly, in order that the gas may not carry away too much water with it. The operator then allows so much hydrogen gas to pass into the mixture that the volume is enlarged from one to three, that is to say, one volume of the gaseous mixture employed for analysis must be mixed with two volumes of hydrogen gas. This quantity of hydrogen gas is sufficient, should the mass of gas consist of oxygen without nitrogen, to convert the whole of it into water. When, however, atmospheric air, which contains nearly four volumes of nitrogen gas to one volume of oxygen gas, is to be examined, the operator employs a smaller proportion of hydrogen gas. It is then sufficient to add as much hydrogen as is equal to half the bulk of the gaseous mixture. When the hydrogen has been added, and the resulting mixture accurately measured, the electric spark is passed through. The consequent diminution of bulk, on being divided by three, gives, as usual, the volume of the oxygen gas contained in the mixture. The difference between the bulk of the oxygen gas and that of the original mixture, is the volume of the nitrogen gas.

In the analysis of atmospheric air, it is scarcely necessary to make any correction for the vapour produced by the explosion of the mixture; because, the atmospheric air employed is seldom quite dry, and the hydrogen gas which is added to it is generally saturated with vapour.

Analysis of a Gaseous Mixture of Oxygen, Hydrogen, and Nitrogen.—When the gaseous mixture consists of oxygen, hydrogen, and nitrogen, the first operation consists in sending the electric spark through a measured portion of it, without the previous addition of any other gas. After detonation, the nitrogen gas remains behind, in company either with oxygen gas or hydrogen gas. The operator adds oxygen gas to the remainder, and again passes the electric spark through the mixture, to ascertain if a farther reduction of volume can be thus effected. If a fresh diminution of volume take place, then the mixture remaining after the first detonation consisted of nitrogen gas and hydrogen gas. In this case, the composition of the gaseous mixture can be easily calculated. But if no reduction of volume takes place when the electric spark is passed through the second time, then the gases which remained after the first explosion were nitrogen and oxygen. A portion of hydrogen gas is then added to the mixture, and another explosion is produced. When the volume of the oxygen gas has been calculated from the diminution of volume produced by the explosion, the quantity of the pure oxygen gas previously added to the mixture must be deducted from the result.

Various other processes have been recommended for the analysis of these gaseous mixtures, and particularly for the analysis of atmospheric air; but, as they afford less accurate results than the method here described, they may be passed over. The substances which are most in use as absorbents of oxygen gas, are phosphorus, nitrous gas, and sulphuret of potassium.

Quantitative Estimation of Water.—The compound of oxygen and hydrogen, or water, is a body so widely disseminated, that its quantitative estimation is of the highest importance.—The estimation can be effected by different processes, the choice of one or the other of which must be made according to the nature of the substances with which the water is combined. The most usual method of determining the quantity of water, is, that of igniting a weighed portion of the compound containing it, in a platinum crucible. The water is then volatilized. When the crucible is cold, the residue is weighed, and the quantity of the water is ascertained from the loss of weight. This method can always be employed when the compound combined with water, experiences no alteration in composition on being heated to redness, but merely loses its water. It is by this process, that the quantity of water of crystallisation in a great number of salts is estimated. The platinum crucible in which the salt has been weighed, is closed with its cover, and very slowly heated. The more water of crystallisation the salt contains, the more slowly must the heating be effected, in order that no loss may be occasioned by spirting. When the quantity of water is so great that the salt melts when exposed to but a low degree of heat, as, for example, is the case with many of the soda salts, then the platinum crucible which contains the salt must be exposed for a considerable time to an extremely gentle degree of heat. The salt may thus be kept from running into a liquid. When the greater part of the water is expelled, the heat is gradually increased, until the whole is finally ignited. The crucible is afterwards weighed. When the dry salt in the platinum crucible is not susceptible of being decomposed by the heat afforded by the spirit lamp with double current of air, it should be ignited over the spirit lamp as strongly as possible; because, many salts retain small quantities of water with much obstinacy. This is the case with arseniate and phosphate of soda. Too long an ignition, however, often produces a partial decomposition of the substance submitted to experiment. This is the case with many salts containing sulphuric acid and metallic oxides. Such compounds must only be exposed to a dull red heat.

Separation of Water from Salts which are affected by Atmospheric Air.—There are many salts, however, which, on being deprived of their water by ignition in a platinum crucible, even when the latter is closed with its cover, acquire from the atmosphere, either an extra dose of oxygen, or a portion of carbonic acid. The former takes place on the ignition of hydrous salts of protoxide of iron; the latter occurs on the ignition of various basic salts. When substances of this description are to be separated from water, they must be placed in a little retort, by which they are sheltered from the air during the ignition. The mode of operating is as follows: A glass bulb is blown at the end of a glass tube, so as to produce a small matrass. It is necessary to employ a tube of strong glass for this purpose, in order that the glass of the bulb may not soften on the first application of the heat. The bulb is weighed. Such a quantity of the hydrous substance is then placed in it as the operator chooses to employ. The glass tube is cleansed from loose particles of the substance by the plume of a feather, and the whole is then weighed. The operator now knows how much of the compound is employed in the experiment. When this has been done, the tube of the little matrass is drawn out to a point, at about half an inch from the bulb, and is then bent on one side so as to form a little retort. This is again weighed. The bulb of the retort is now gradually ignited, and the heat is made as powerful as the glass can endure. The volatilized water must be wholly expelled from the neck of the retort, by the flame of a small spirit lamp. When no fresh portions of aqueous vapour are deposited in the neck of the retort, the point of the neck must be quickly melted and closed, by the flame of a small spirit lamp, while the ignition of the bulb of the retort is continued. The operator must be careful to lose none of the glass in closing the point. The whole is then permitted to become perfectly cold; the point is then carefully filed off, and the retort with the point are weighed. The loss of weight indicates how much water the substance has lost by the ignition.—As the compound is allowed to cool where atmospheric air has no access, it can neither become more highly oxidised, nor contaminated by carbonic acid. But, as the point of the retort is closed during the ignition, the air enclosed in the retort is extremely rarefied. If, therefore, the point were not broken off previous to the weighing of the retort, too great a loss of weight would be experienced, and too great a quantity of water would be ascribed to the subject of the experiment. It is, consequently, necessary to allow the retort to become full of air, which has no action on the contents when the whole is perfectly cold.

Separation of Mother-liquor from Salts.—The perfectly-accurate estimation of the water of crystallisation in salts is combined with the greatest difficulties. Besides water of crystallisation chemically combined, all salts which have been separated by crystallisation from aqueous solutions contain water enclosed mechanically between their particles. The greater or smaller quantity of this accidental water depends on the largeness or smallness of the crystals. This water is part of the mother-liquor enclosed in the substance mechanically. The quantity often amounts, in large crystals, to several per cents; but, in very small crystals, it commonly amounts to only a half per cent. The greater portion of it can be separated from the salt, by laying it in powder upon bibulous paper, exposed to the temperature of 90° or 100° Fahrenheit. If the salts are given to effloresce, like many soda salts, they must be examined immediately upon being pulverised, that they may not also lose their combined water. If the salt is deliquescent, it must be dried by being laid between a considerable quantity of bibulous paper, and submitted to the action of a press. The paper must be renewed as long as it continues to become moist. When the salt is dry, it is instantly employed for the experiment.

Separation of Water of Decrepitation from Salts.—A great many salts contain no water of crystallisation, but when they have been crystallised from an aqueous solution, retain a portion of water mechanically enclosed in their crystals. When these salts are not decomposed by ignition, they can be deprived of this accidental water by being heated to redness before they are subjected to analysis. But when they are liable to be decomposed by ignition, which is the case with the anhydrous nitrates, they must only be strongly heated when the water is to be expelled. In general, the whole of these salts decrepitate with violence on being heated, particularly if the crystals are large. A considerable portion of the salt intended for analysis can, therefore, be lost, unless the ignition be performed in a crucible which can be accurately closed. The decrepitation, however, is rendered much less violent if the salt be previously reduced to a very fine powder, and the powder be exposed for some time to a moderate heat. —Some of the salts which contain water of crystallisation are likewise subject to decrepitate on being heated, in consequence of the presence of extraneous water. These, however, are either salts which contain but little water of crystallisation, such as bicarbonate of potash, or salts which contain only that portion of water which is essential to their existence, such as hypophosphite of lime. When the latter salts are deprived by heat of their water of crystallisation, the salts are simultaneously decomposed.

Separation of Water of Crystallisation from Salts which cannot be ignited.—Many salts which contain water of crystallisation are decomposed at an incipient red heat, so that it is impossible to determine the quantity of water they contain from the loss of weight occasioned by exposing them to a strong heat. Some of these salts, for example, the nitrates, can, nevertheless, be entirely deprived of their water by being strongly heated, though at a temperature inferior to ignition. In such a degree of heat, the acid escapes decomposition.—Other salts, however, particularly those in which the bases are combined with organic acids, cannot even be so strongly heated, without suffering decomposition. To render these salts anhydrous, they must be finely pulverised, and placed near sulphuric acid, under the receiver of an air-pump, which is then to be exhausted of air. When the whole has remained in this state for some time, the salt is removed and weighed. The loss of weight indicates the quantity of water of which it has been deprived by the sulphuric acid. The salt is replaced under the exhausted receiver, and allowed to remain again for some time exposed to the absorbent action of the sulphuric acid. It is then weighed a second time. If the result of the second weighing agrees with that of the first weighing, it is a proof that the first drying had been sufficient to deprive the salt of the whole of its water. But, if the two weighings do not agree, the salt must be exposed a third time to the action of sulphuric acid in vacuo. In short, this operation must be repeated until the agreement in the results of the two last weighings shows that the salt has become completely dry. The loss of weight indicates the quantity of water.

Many of these salts, however, retain their water of crystallisation, or at least a portion of it, with such a degree of obstinacy, that it is impossible to render them anhydrous by this process. In many cases, the water of crystallisation can then be determined as follows: The vessel containing a weighed portion of the finely-pulverised salt, is placed in a capsule filled with hot sand. The temperature of the sand must, however, not be so high as to cause the decomposition of the salt. The capsule is then placed near a vessel of sulphuric acid under the receiver of the air-pump, and the air is quickly pumped out. After some time, the salt is weighed, and again placed in the same manner under the receiver of the air-pump. When it has remained there for some time, it is once more weighed. The operation is repeated until the two last weighings give the same result.

The water of crystallisation is essential to the existence of some salts, so that upon being heated they are decomposed before they lose their water. The estimation of the quantity of the water of crystallisation is, in such cases, accompanied by many difficulties. In general, it is calculated from the products of the decomposition of the salt. No universal rule can be given in this case; for the methods to be employed must be chosen according to the nature of the constituents of the salts which are to be examined. All the phosphites and hypophosphites are salts of this nature. The manner in which it is necessary to operate, in determining the quantity of water contained in these substances, has been described at page 266.

Quantitative Estimation of the Water in Hydrous Acids.—Water is found in combination, not only with salts, but with most acids; and in most cases, the hydrous acids hold it so fixedly, that a heat sufficient to volatilize water with ease is incapable of separating it from acids. The reason of this is, that in the hydrous acids the water supplies the place of a base, and in general contains the same quantity of oxygen as the base with which the acid forms a neutral salt. To ascertain, therefore, the quantity of the water, a weighed quantity of the hydrous acid is saturated with a base with which it is capable of forming an anhydrous salt. The base then combines with the acid and separates the water. The resulting anhydrous salt is then weighed. If the weight of the base is known, it is only necessary to deduct the weight of the resulting anhydrous salt from the common weight of the base and the hydrous acid, to ascertain the quantity of water contained in the acid employed.—The base employed in this experiment, in nearly all cases, is recently-ignited protoxide of lead. This substance is better adapted to the purpose than earths and alcalies, because it does not so rapidly attract carbonic acid. The weighed portion of the hydrous acid is dissolved in water and the protoxide of lead is added in excess. The whole is evaporated to dryness, and the dry residue is heated to redness. But in that case, the acid in the lead salt must be one of those which mere ignition is unable to destroy. If the acid is capable of being destroyed by this mode of treatment, the salt must merely be exposed for a considerable time to a moderate heat, to get rid of the water. The difference in weight between this ignited or dried lead salt with excess of protoxide of lead, and the common weight of the hydrous acid and protoxide of lead employed in the experiment, indicates the quantity of water contained in the hydrous acid.

If the hydrous acid forms with a base a compound which is neutral, anhydrous, and completely insoluble in water, the estimation of the water may be effected as follows. The aqueous solution of a weighed portion of the hydrous acid is mixed with a solution of a salt of this base. The resulting neutral insoluble salt is collected and weighed, and the quantity of the water is then calculated. It is only the different hydrates of sulphuric acid, however, that can be estimated by this process. A weighed quantity of the hydrous acid is diluted with a large quantity of water and precipitated by a solution of chloride of barium. The resulting sulphate of barytes is dried and weighed. The quantity of the sulphuric acid is thus ascertained and thence also the weight of the water which was previously combined with it.—Various other acids, as, for example, phosphoric acid, arsenic acid, &c., combine also with bases to form salts which are insoluble in water; yet the quantity of water contained in these acids cannot be estimated by the above process. The reason of this is, that these acids are capable of producing a variety of insoluble salts; so that when a precipitate is formed by a base, it does not consist of a pure neutral compound, but is very often contaminated by a variety of basic compounds. This is the case even when the dissolved acid has been accurately neutralized by ammonia. The consequence of this is, that it is afterwards necessary to determine by another operation, how large a quantity of the base the precipitate contains. This is accompanied by additional difficulties, and, after all, one cannot always obtain a very accurate result, since the resulting compound is often not quite insoluble in water. It is always best, therefore, to determine the quantity of water contained in these acids by means of protoxide of lead. This subject has been already treated of at pages 198 and 249.

When the hydrous acid for examination is in the solid state, it is only necessary to mix a weighed portion of it with a weighed portion of recently-ignited protoxide of lead and to heat the mixture to ignition, provided the resulting compound is not decomposable by a red heat. The quantity of water is then ascertained from the loss of weight. If the acid forms, with the protoxide of lead, a compound which easily fuses, as is very often the case, the operator need only lay the protoxide of lead over the acid in the platinum crucible, and then cautiously heat the mixture. If the resulting salt of lead is liable to be decomposed when exposed to ignition in the air, the experiment must be effected in a retort. The operator must take care, in that case, not to employ too strong a heat, lest the protoxide of lead should act upon the glass.

Separation of Water from Hydrated Oxides.—Many bases also contain water in a state of chemical combination. From some of these it can be expelled by a strong heat; but from others, for example from potash and soda, it cannot be expelled even by the strongest heat. In the latter case, the quantity of the water is estimated as follows: A weighed quantity of the hydrate is dissolved in a small portion of water, and the solution is supersaturated by an acid which forms a neutral salt with the base. The solution is evaporated to dryness, and the dry mass is ignited to expel the excess of acid. The operator may employ sulphuric acid for this experiment, but muriatic acid is the best; because an excess of sulphuric acid is much more difficult of accurate separation from sulphate of potash or sulphate of soda, than an excess of muriatic acid from chloride of potassium or chloride of sodium. From the weight of the anhydrous neutral sulphate or chloride, the operator can easily calculate the equivalent quantity of dry alcali, and consequently the weight of the hydrate water.

It is scarcely possible to give any farther general directions for determining the quantity of water in compounds. In the preceding sections, those methods have always been taken into consideration, according to which the determination of the water contained in various compounds must be effected, when the usual method of determination by the ignition of the compound is not practicable.

Quantitative Estimation of Ammonia in Ammoniacal Salts.—The method of analysing a mixture of nitrogen gas and hydrogen gas has been described above. It remains now to show in what manner the chemical compound of nitrogen and hydrogen, the alcali ammonia, can be separated from other substances and quantitatively estimated. This analysis is often attended with many difficulties. The most accurate result is obtained in the analysis of the ammoniacal compounds, by determining experimentally the quantity of the substances combined with the ammonia, and then estimating the ammonia from the loss experienced. As the methods of quantitatively estimating the inorganic acids have been fully treated of in the foregoing sections, it is unnecessary to state here in what manner the determination of the acids contained in the soluble salts of ammonia should be effected.

When the acid contained in a weighed quantity of the ammoniacal salt has been quantitatively determined, the loss of weight indicates, not merely the quantity of the ammonia, but the common weight of the ammonia and the water of the salt. All the compounds which are formed by ammonia with oxygen acids, contain water, of which at least a portion is invariably necessary to the existence of the compound, and cannot be expelled without decomposing the compound.

When the operator desires to estimate the quantity of the ammonia contained in a compound, the compound must be decomposed, with the aid of heat, by a weighed quantity of a strong base, and the quantity of the disengaged water must be determined. After the decomposition, the increase of weight of the strong base indicates the quantity of the acid which was previously combined with the ammonia. This gives the common weight of the ammonia and the disengaged water. If, then, the quantity of the water has been separately determined, the quantity of the ammonia can be easily calculated. It is also possible, however, to determine directly the quantity of the ammonia. With this view, it must be led into muriatic acid, and the resulting muriate of ammonia must be estimated experimentally.

When the quantity of the ammonia is to be estimated from the loss of weight, and that of the disengaged water by direct experiment, the operator must proceed as follows: The portion of the ammoniacal salt which is to be analysed is put into a little matrass, such as has been represented at page 324. As this matrass must be formed of very strong glass, it cannot be made of a glass tube, but must be obtained at the glass-house. For want of such a matrass, the operator employs a small retort. When the weight of the matrass or retort has been determined, an indeterminate quantity of the finely-pulverised salt is shaken into it; the neck of the vessel is cleansed with the plume of a feather, and the whole is again weighed. The operator thus ascertains how much of the salt is employed in the experiment. He then introduces into the matrass a quantity of pure caustic lime in fine powder. Calcined Carrara marble answers the purpose best. Rather more than twice the weight of the ammoniacal salt should be taken. The two substances are mixed together as accurately as possible, by shaking the retort, and the vessel is afterwards weighed anew. The neck of the matrass is then drawn out to a fine point, and is bent in such a manner as to bring the matrass into the shape of a retort. When a retort is employed, the neck must still be drawn out to a point. After the neck has been drawn out, the matrass or retort is weighed for the fourth time. The neck is then connected by means of a tube of caoutchouc with a little receiver *b*, in the manner which is represented at page 324. This receiver must be quite filled with pieces of caustic potash, and must be connected with a little glass tube *c*, also filled with caustic potash. The glass tube *c*, the receiver *b*, and the caoutchouc tube are previously weighed. When the apparatus is placed together, the glass bulb is gradually heated. The heat is afterwards increased till it is as powerful as it can be made. The ammonia gas is very soon expelled; but a portion of the water is retained with much obstinacy by the excess of lime and the resulting salt of lime, and can only be separated by the application of an extremely strong heat. When the glass bulb is of very small circumference, the ignition can be effected over a spirit lamp with circular wick; but when the vessel is of a larger size, it must be heated in a small furnace over a free charcoal fire. When the whole is cold, the neck of the retort is cut off at *d*, and the retort is weighed. The receiver, the glass tube, and the point of the retort, are weighed together. The point is then dried and weighed alone; its weight is deducted from the weight of the receiver, and added to the weight of the retort. The loss of weight experienced by the retort, in consequence of the ignition, indicates the common weight of the ammonia and the water. The increase of weight experienced by the caustic potash, indicates the quantity of water expelled from the ammoniacal salt employed in the experiment. The difference is the weight of the ammonia.

This experiment is attended by a very disagreeable circumstance. The heat required to expel the whole of the water from the retort is so great as frequently to effect the fusion of the vessel. When, farther, the ignition is performed in a furnace, over a free fire, it often happens that after cooling, the retort is not in a fit state to be weighed with that extreme accuracy which is absolutely essential. But, now, since the ammonia can be completely expelled from the apparatus by a very moderate degree of heat, and it is only the perfect expulsion of the water which requires so very high a temperature, it becomes advisable to perform the experiment as follows: The operator heats the retort merely by the flame of a spirit lamp with circular wick. He then allows the whole to cool, and afterwards determines the weight of the retort, and of the receiver and glass tube in the manner described above. The loss of weight experienced by the retort is equal to the whole of the ammonia and a portion of the water. The increase of weight of the caustic potash indicates the weight of this portion of water. If, therefore, the increase of weight of the caustic potash is deducted from the loss of weight of the retort, the difference shows with great accuracy the weight of the ammonia expelled from the ammoniacal salt submitted to experiment.

When only small quantities of the ammoniacal salts are submitted to experiment, as, for example, portions of 20 or 30 grains, it is unnecessary to employ the receiver *b*. It is sufficient to connect the neck of the retort, by means of a cork, directly with the tube containing the caustic potash.

When the heat employed in this experiment is sufficiently powerful to expel the whole of the water from the calcareous salt in the retort, it is possible to ascertain not only the weight of the water, but even that of the ammonia.

To this end, the neck of the retort is connected with a glass tube filled with caustic potash, and the latter is connected by a caoutchouc tube with another glass tube filled with chloride of calcium. Both of these glass tubes must be weighed separately before the experiment. The increase of weight sustained by the caustic potash will indicate the quantity of the water. The increase of weight of the chloride of calcium will indicate the quantity of the ammonia expelled from the ammoniacal salt submitted to analysis. It has not been determined by experiment, however, whether the results afforded by this method are accurate.

In some cases, it is possible to determine the common weight of the ammonia and the water, from the loss of weight experienced on subjecting the substance to a simple ignition. This occurs in the case of some of the double salts formed by the combination of an ammoniacal salt with another salt having a fixed base. When such a double salt is ignited, the acid of the ammoniacal salt combines with the salt of the fixed base, and forms an acid salt. This is the case, for example, with the double salts formed by phosphate of ammonia or arseniate of ammonia with the phosphates or arseniates of other bases.—Other ammoniacal salts also, the acids of which in a state of purity are either completely fixed in the fire, or only capable of decomposition by a very strong heat, can be completely and safely decomposed by gentle ignition in open vessels. The common weight of their water and ammonia can, therefore, be readily determined. Salts of this description are those formed by the combination of ammonia with titanic acid, molybdic acid, tungstic acid, antimonic acid, antimonious acid, tantalic acid, &c. Some few of these compounds, if ignited in close vessels, where atmospheric air has no access, are decomposed in such a manner that the acid is reduced to a lower oxide. This arises from the decomposition of the ammonia.

The experimental determination of the ammonia contained in ammoniacal salts, can also be effected by leading the gas into muriatic acid, and calculating the quantity of ammonia from the weight of the resulting sal ammoniac.

The method of operating is as follows: A weighed portion of the ammoniacal salt is dissolved in a matrass in a small quantity of water. The neck of the matrass is closed air-tight by a cork through which a glass tube is passed. The tube passes but a very little way into the matrass; above the cork it is bent at a sharp angle, so that the other end can pass nearly to the bottom of a cylindrical glass vessel, which must be about a foot high, and one or two inches in diameter. Another cork is fastened on this glass tube, and fixed into the mouth of the cylindrical vessel, which, however, must not be closed air-tight. Such a quantity of diluted muriatic acid is then poured into the cylinder, that the end of the glass tube stands about two inches below the surface of the acid. When the apparatus is placed together, the operator pours into the matrass, either a solution of caustic potash, or barytic water; of one or the other such a quantity as shall afford base in sufficient excess to effect the entire decomposition of the salt of ammonia. The matrass is then placed in a sand-bath. The ammonia volatilizes at a very gentle heat, and passing into the cylinder, combines with the muriatic acid and produces muriate of ammonia. At first, when not only ammonia, but atmospheric air passes from the matrass into the cylinder, the escape of the atmospheric air causes clouds of muriate of ammonia to rise from the muriatic acid into the upper part of the cylinder. When, however, the operation is properly conducted, these clouds only proceed about half way up the cylinder, and then sink back into the solution in consequence of their heaviness; nothing, therefore, is lost. The temperature is then gradually increased; but it often happens, at this period of the process, that the mass in the matrass begins to foam violently, instantly boils over, and of course spoils the experiment. This is particularly the case, when caustic potash is employed, on which account the use of barytes water is preferable.

When the ammonia has been driven over, the boiling of the liquid in the matrass must be continued until at least half the water is distilled over. It is necessary to do this, to drive all the ammonia out of the matrass into the cylinder, by means of the aqueous vapour produced. But as, towards the end of the process, when scarcely any more ammonia is produced, the solution very easily rushes back from the cylinder into the matrass, more especially when the heat applied to the matrass is not perfectly uniform, it is proper, when the operation is nearly at an end, to raise the glass tube out of the muriatic acid, and to bring the mouth of it immediately above the surface of the acid. The danger of spoiling the experiment is thus avoided.—The muriatic acid is poured from the cylinder into a small counterpoised platinum capsule, and is very carefully evaporated to dryness, by a heat so gentle that no muriate of ammonia can volatilise. The heat applied must, therefore, never exceed that of the boiling point of water. When the mass is apparently dry, the platinum capsule with the muriate of ammonia is weighed. The capsule is then again gently warmed, to drive away the last traces of muriatic acid and water, and is afterwards weighed anew. This operation is repeated until the two last weighings agree. It is easy to calculate, from the weight of the resulting muriate of ammonia, the quantity of ammonia contained in the salt submitted to analysis.

The methods above described are adapted not only to the analysis of the compounds of ammonia with oxygen acids, but also to those of ammonia with hydrogen acids; or, what is the same thing, to the compounds of ammonium (1 nitrogen + 4 hydrogen) with chlorine, bromine, and iodine. Although the latter contain no water of crystallisation, yet it is well known that water is produced when they are decomposed by bases. The water results from the combination of the oxygen of the base with the hydrogen of the acid or the ammonium. The same phenomena are produced in the quantitative estimation of the constituents of these compounds, as in the quantitative estimation of the ammoniacal salts produced by oxygen acids.

Separation of Ammonia from other Gases.—When gaseous ammonia is mingled with other gases, it can be separated by water, provided the other gases be not soluble in water. Gaseous ammonia can also be very well separated from all other gases with which it can occur in mixture, by means of dry chloride of calcium.

Separation of Hydrogen from Chlorine, Bromine, Iodine, and Cyanogen: Analysis of Muriatic, Hydrobromic, Hydroiodic, and Hydrocyanic Acids.—The compounds of hydrogen with chlorine, bromine, iodine, and cyanogen, or the muriatic, hydrobromic, hydroiodic, and hydrocyanic acids, supposed to be contained in aqueous solutions, are quantitatively estimated according to methods which have been partly described in preceding sections. The precipitation of muriatic acid is effected by a solution of nitrate of silver. The precipitation of the hydrobromic and hydroiodic acids could also be effected by the same reagent. In the quantitative estimation of the hydrocyanic acid, the solution of nitrate of silver appears likewise to be the best precipitant. From the weight of the precipitated cyanuret of silver, the quantity of the acid in the solution is reckoned. It would probably be safer, to convert the cyanuret of silver into metallic silver by ignition, and to reckon from the weight of the silver the quantity of the cyanuret of silver, and thence that of the hydrocyanic acid. It is necessary, in this case, that the solution of hydrocyanic acid contain no muriatic acid. The above method of effecting the quantitative estimation of hydrocyanic acid appears to afford a more accurate result than another which is more frequently employed, and is as follows: The aqueous hydrocyanic acid is first mixed with a solution of potash, then with a solution of iron containing both protoxide and peroxide, and finally with diluted muriatic acid. A precipitate of Prussian blue is produced, from the weight of which, the quantity of the hydrocyanic acid is calculated.

Separation of Muriatic Acid Gas from other Gases.—When muriatic acid in the gaseous state is mingled with other gases, it can be separated by water, which absorbs it completely and rapidly. The other gases must, however, be insoluble in water. To separate muriatic acid gas from carbonic acid gas, pieces of dry borax are put through the mercury into the gaseous mixture. The borax absorbs the muriatic acid gas, but does not act on the carbonic acid gas.

Analysis of the Compounds of Hydrogen and Carbon.—The compounds formed by hydrogen and carbon are partly gaseous, partly liquid, partly solid. They frequently occur in combination with one another, in which cases the analysis is accompanied by difficulties. When the two gaseous compounds of carbon and hydrogen, the carburetted hydrogen gas in minimum of carbon (gas of marshes, fire-damp), and the carburetted hydrogen gas in maximum of carbon (olefiant gas), occur together, as they do in the gaseous mixture obtained by the distillation of coal and oil, and employed in gas-lighting, they can be separated from one another, according to HENRY (*Annales de Chimie et de Physique*, T. XVIII. p. 72), by the following process: The gaseous mixture is treated with chlorine gas. Chlorine gas combines, in darkness, with olefiant gas alone, producing chlorine ether; but, in the sunshine, it combines with the gas of marshes, producing muriatic acid and carbonic acid. The separation of the two sorts of carburetted hydrogen gas can be effected, of course, only over water, because chlorine gas is absorbed by mercury. The operator first passes chlorine gas into a graduated glass tube over water, and measures the volume of the chlorine. He then permits the gaseous mixture for examination, which must previously have been measured in another graduated glass tube, to rise into the tube and mix with the chlorine gas. The more olefiant gas the mixture contains, the less chlorine gas is necessary to be added to it; because only one volume of chlorine gas is required to combine with one volume of olefiant gas, to produce chlorine ether. In order that the action of the chlorine may take place in darkness, it is best to cover the glass tube with a paper case; but when the experiment is performed by candle-light, this precaution is scarcely necessary. When the gaseous mixture has reposed for a quarter of an hour, all the chlorine ether will have separated. The quantity of the olefiant gas is then calculated from the diminution of bulk of the gaseous mixture. Half the quantity which disappears is the volume of the olefiant gas. The mixture is then exposed to the rays of the sun, or merely to full day-light, whereupon the gas of marshes is converted by the chlorine gas into muriatic acid gas, which is completely absorbed by the water, and carbonic acid which continues in the gaseous state. The decomposition is effected more rapidly by the rays of the sun than by mere day-light. If an excess of chlorine gas has been employed in this experiment, then the gas remaining after the decomposition, and which consists of carbonic acid gas and chlorine gas, will be completely absorbed by a solution of caustic potash. This is not the case when too small a quantity of chlorine gas has been employed, because the carbonic oxide gas then produced is not absorbable by caustic potash. Neither is it the case when the gaseous mixture submitted to examination contains other gases than those composed of carbon and hydrogen. Four volumes of chlorine gas are required to convert one volume of carburetted hydrogen in minimum of carbon, into carbonic and muriatic acids.—This method of separation cannot give such accurate results as are obtained in the analysis of other gases. As the experiment must be performed over water, the carbonic acid and the chlorine gas are partly dissolved before the volume of either can be properly measured. If an attempt to avoid this be made by using water saturated with chlorine, then a portion of chlorine ether is formed while the measured volume of gas for examination is passed through the liquid into the tube, whereby another source of error is produced. Finally, a portion of gaseous chlorine ether is formed after the absorption of the olefiant gas in the dark, on which account the volume of the gas not absorbed in the dark, appears larger than it should do.

If one volume of carburetted hydrogen gas in minimum of carbon, is mixed in a glass tube such as is represented at page 383, with rather more than twice its volume of oxygen gas, and is then exploded by the electric spark, it is wholly converted into water and carbonic acid. The resulting carbonic acid gas occupies the same bulk as the decomposed carburetted hydrogen gas. After the explosion, the resulting carbonic acid gas is separated from the excess of oxygen gas in the usual manner, namely, by absorption by caustic potash.—If a volume of carburetted hydrogen gas in maximum of carbon, is exploded in a similar manner with rather more than three times its volume of oxygen gas, it is likewise completely converted into water and carbonic acid gas; but, in this case, the volume of the resulting carbonic acid gas is twice as large as the volume of the carburetted hydrogen gas submitted to experiment.—When a gaseous mixture consists of the two sorts of carburetted hydrogen gas, its volume is first accurately measured, and it is then exploded with oxygen gas. The operator can then very easily find the proportions of the mixed gases from the resulting volume of carbonic acid gas. After the explosion, caustic potash is introduced into the glass to absorb the carbonic acid. The diminution of bulk thus produced, indicates the volume of the carbonic acid gas. This must always be larger than the volume of the gaseous mixture submitted to analysis. The excess corresponds exactly with the volume of the olefiant gas contained in the gaseous mixture. Knowing this, the volume of the gas of marshes can easily be calculated. If, for example, the gaseous mixture amounted to 50 volumes, and the carbonic acid gas to 80 volumes, then the gaseous mixture contained 30 volumes of olefiant gas, and 20 volumes of gas of marshes.

The performance of this experiment is attended with danger, particularly when the gaseous mixture contains much olefiant gas. The decomposition is accompanied by so violent an explosion, that the thickest glass tubes are shattered to pieces with facility. It is proper, therefore, to explode but a small quantity of the gas at once, and to wrap a cloth about the glass tube previous to the explosion.

If the gaseous mixture contains free hydrogen gas, the results afforded by the above method of analysis, are by no means accurate.

Analysis of Gaseous Mixtures, containing the two sorts of Carburetted Hydrogen, with Hydrogen, Carbonic Oxide, Carbonic Acid, and Nitrogen.—The gaseous mixtures which contain the two sorts of carburetted hydrogen gas, can also contain free hydrogen gas, carbonic oxide gas, carbonic acid gas, and nitrogen gas. These six gases can be separated from one another by the following process: The volume of the gaseous mixture is first measured over mercury. The carbonic acid gas is then removed by a piece of moistened caustic potash, which is fastened on an iron wire, and pushed through the mercury into the gas. After absorption, the potash is drawn out, and the volume of the carbonic acid gas is estimated from the diminution of bulk. The operator then introduces potassium into the upper part of the tube, which must be held in an inclined position, and heated. The potassium, if added in sufficient quantity, decomposes the carbonic oxide gas completely, but does not act on the other gases. The carbon of the carbonic oxide gas is deposited upon the potassium, while the oxygen belonging to it enters into combination with the potassium. The diminution of the bulk of the gas intimates the volume of the carbonic oxide. A measured volume of the residual gas is then treated over water in darkness with chlorine gas, in the manner described above. The olefiant gas is thus removed. The residue is then exposed with chlorine gas to day-light; upon which, the gas of marshes, and the free hydrogen gas, both combine with chlorine. The mixture must not be exposed to the direct rays of the sun, for if much free hydrogen be present, an explosion may be occasioned. The gas of marshes leaves carbonic acid. The muriatic acid gas produced by the combination of the chlorine with the hydrogen of the gas of marshes, and with the free hydrogen, is absorbed by the water. The residual gas is shaken with mercury, which separates the excess of chlorine. The carbonic acid gas is then absorbed in the usual manner by caustic potash, and its volume is ascertained. Hereby, the quantity of the gas of marshes is ascertained; for its volume is equal to the volume of the resulting carbonic acid gas. The remainder consists of nitrogen gas, which is now measured. The volume of the free hydrogen gas is ascertained from the loss.—It will be understood, that this operation cannot give very accurate results. Nevertheless, the results obtained approach the truth pretty nearly; and, since the examination of such gaseous mixtures is almost always undertaken for merely technical purposes, the results obtained by this mode of experimenting may be considered as sufficiently accurate.

Analysis of a Gaseous Mixture, containing Gas of Marshes, Carbonic Acid, Nitrogen, and Oxygen.—When the carburetted hydrogen gas is not mingled with all the above named gases, but only with some of them, the analysis can then be performed in a simpler manner. The gas of marshes commonly contains not only carburetted hydrogen gas in minimum of carbon, but carbonic acid gas and atmospheric air, or rather nitrogen gas and oxygen gas. The volume of the carbonic acid gas is found by absorption by caustic potash. The volume of the oxygen gas is, in the present instance, best ascertained by means of phosphorus, which absorbs it with sufficient accuracy. The phosphorus is placed in the upper part of the glass tube after the removal of the potash. The residual gas is afterwards mixed with chlorine gas over water, and exposed to day-light, to decompose the carburetted hydrogen. The resulting carbonic acid gas, and the excess of chlorine gas, are removed by potash. The residue is nitrogen gas.

Decomposition of the Compounds of Carbon and Hydrogen, by Ignition with Oxide of Copper.—To determine with accuracy the proportion of the elements in the many compounds of carbon with hydrogen, it is best, whether the compound be solid, liquid, or gaseous, to convert it into water and carbonic acid, by ignition with deutoxide of copper. The method of operating will be fully described in a subsequent paragraph.

Analysis of the Compounds of Phosphorus and Hydrogen.—The compounds of hydrogen with phosphorus, which are all gaseous, can be best analysed as follows: A weighed quantity of dry chloride or sulphuret of copper is exposed to a very gentle heat, and the phosphuretted hydrogen gas is in the mean time passed over it. The hydrogen of the phosphuretted hydrogen gas combines with the chlorine to form muriatic acid gas, or with the sulphur to form sulphuretted hydrogen gas, which, in either case, flies away. The phosphorus, in the mean while, combines with the copper to form phosphuret of copper, which remains wholly behind. The phosphuret of copper contains more or less phosphorus, according as more or less of that element was contained in the phosphuretted hydrogen gas. From the weight of the resulting phosphuret of copper, the quantity of copper in which is known, since the experiment is performed with a weighed portion of chloride or sulphuret of copper, the composition of the phosphuretted hydrogen gas can be calculated. The spontaneously inflammable phosphuretted hydrogen gas always contains hydrogen gas in a state of mere admixture. The sulphuret of copper is, however, not at all attacked by hydrogen gas; nor is the chloride of copper or the resulting phosphuret of copper affected by hydrogen gas, except at a temperature much higher than any which need be employed in the experiment.

Analysis of the Gaseous Compound of Sulphur and Hydrogen.—The gaseous compound of sulphur and hydrogen, called sulphuretted hydrogen gas, is quantitatively estimated by the process already described at page 228. When the volume of this compound, which may exist in a gaseous mixture, is to be determined, the gas may be fully absorbed by various substances. The absorption is best effected in the same manner as the absorption of carbonic acid gas. A piece of moistened caustic potash is fastened on the end of a thin iron wire and passed through the mercury into the gaseous mixture. The sulphuretted hydrogen gas is thus completely absorbed. But if the gaseous mixture contains other gases also susceptible of complete absorption by caustic potash, as, for example, carbonic acid gas, and some other gaseous acids, then the sulphuretted hydrogen gas must be absorbed by acetate of lead strongly moistened with acetic acid, or instead of that, by a concentrated solution of acetate of lead mixed with acetic acid, which is incapable of absorbing carbonic acid gas. When muriatic acid gas and sulphuretted hydrogen gas exist in mixture together, they may be separated by a very small portion of water. This very easily dissolves the muriatic acid gas, but takes up a far smaller quantity of the sulphuretted hydrogen gas. Since, however, the sulphuretted hydrogen gas is in some measure dissolved by the water, it is better to employ borax to separate these two gases. This is a method which has been recommended by CLUZEL (*Annales* *de Chimie*, LXXXIV. p. 110). Borax easily absorbs muriatic acid gas, even when it is employed in lumps. It would also be possible to separate sulphurous acid gas from carbonic acid gas by using borax, which absorbs all the strong acid gases but not others; yet the method described at page 310, of separating these two gases by brown oxide of lead, is still preferable.

In all experiments with sulphuretted hydrogen gas over mercury, it must be borne in mind, that this gas is decomposed, even in the cold, though slowly, by the mercury. Sulphur is absorbed and hydrogen set at liberty. The volume of the gas remains unchanged.

Precipitation of Sulphuretted Hydrogen.—When sulphuretted hydrogen is dissolved in a liquid, it can be best estimated by precipitation. The liquid is mixed with the solution of a metallic oxide, with which the sulphuretted hydrogen can form an insoluble sulphuret. The operator can employ for this purpose a solution of nitrate of silver, or of perchloride of copper. The use of acetate of lead is less advisable. When the resulting sulphuret has been separated, it is proper to treat the sulphuret of silver or sulphuret of copper with fuming nitric acid. Complete oxidation should be effected. The sulphuric acid thus produced is then precipitated by a salt of barytes as sulphate of barytes. The operator determines the weight of this precipitate, and calculates thence the quantity of the sulphuretted hydrogen. This method is in every respect preferable to that according to which the quantity of the sulphuretted hydrogen is calculated from the weight of the metallic sulphuret; for if any chlorides were present, the nitrate of silver would not only precipitate sulphuret of silver but chloride of silver. This could be prevented, indeed, by the addition of ammonia; but then other substances might by that means be precipitated.—This method of estimating sulphuretted hydrogen may be employed with good effect in the analysis of sulphurous mineral waters, or in other cases where small quantities of sulphuretted hydrogen gas are dissolved in a liquid. The operator must remember, however, that the presence of metallic sulphurets in solution, as, for example, sulphuret of potassium and sulphuret of sodium, can also precipitate the metallic oxides as insoluble sulphurets.

Separation of Hydrogen from Selenium, Tellurium, and Arsenic.—The gaseous compounds of selenium and tellurium with hydrogen, are so very similar to sulphuretted hydrogen gas that they can be separated from other gases and quantitatively estimated in the same manner as the latter.—With respect to the gaseous compound of arsenic with hydrogen, we have only to observe, that no method of effecting its separation from other gases, and of estimating its quantity, has yet been discovered.

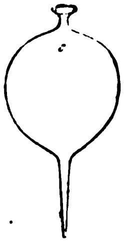
Analysis of Organic Substances.—We have now to treat of the quantitative estimation of the solid, liquid, and even gaseous compounds, containing hydrogen, by means of combustion with chlorate of potash or deutoxide of copper. The substances, of which the composition is thus determined, consist principally of hydrogen, carbon, and oxygen, or of hydrogen, carbon, oxygen, and nitrogen. They are commonly termed organic substances. It has, however, been often remarked in the preceding pages, that many other substances, particularly such as contain carbon, can also be best analysed in this manner.

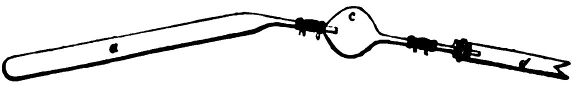
It is impossible to give, in this Manual, any account of the methods of separating organic substances into what are called their proximate elements. What is to be explained here, is the method of resolving organic bodies, with accuracy, into their ultimate elements. The decomposition is effected by oxidising the constituents of the organic bodies, by converting the hydrogen into water, the carbon into carbonic acid. The nitrogen alone can never be oxidised. It is always obtained in the state of nitrogen gas. The water produced in the operation is accurately weighed, and the respective volumes of the resulting carbonic acid and nitrogen gases are measured. The composition of the substance submitted to examination can then be easily calculated. The quantity of the oxygen contained in the substance is almost always best estimated from the loss.

Employment of Chlorate of Potash, in the Decomposition of

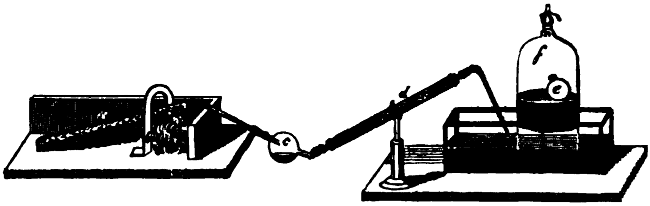
Organic Substances.—**Gay-Lussac** and **Thenard**, as well as **Berzelius**, employed chlorate of potash in their earlier analyses. The substance to be examined was mingled therewith and ignited. The individual constituents of the substance then became oxidised by the oxygen gas set at liberty by the chlorate of potash. **Gay-Lussac** and **Thenard**, who performed the first accurate analyses in this manner, contrived a very ingenious apparatus for the purpose (*Recherches Physico-Chimiques,* T. II. p. 269). But this instrument was of such a nature as not to admit of the direct weighing of the water produced, so that the quantity of the water had to be reckoned from the loss experienced. In consequence of this failure, the quantity of hydrogen contained in the substance submitted to experiment, was determined with far less accuracy than when the resulting water could be weighed. The inventors of the apparatus have therefore of late abandoned the use of it.

According to **Berzelius** (*Lehrbuch der Chemie,* T. III. p. 161), the decomposition by means of chlorate of potash is performed as follows. The substance for examination, either in a state of purity, or combined with oxide of lead, which is the better method, is mixed with chlorate of potash, and put into a long glass tube closed at one end. The tube has an interior diameter of half an inch. The mixing of the substance for examination with the chlorate of potash, is performed in a mortar previously heated to +212° F. or even higher, that it may be perfectly dry. One part of the substance is very accurately mixed with five or six parts of dry chlorate of potash. The mixture is afterwards rubbed together with ten or twelve times its weight of chloride of sodium, recently fused to deprive it of moisture. The mixture must be made with great care, and the mortar must be kept constantly hot during the operation, that no moisture may be absorbed. The mixture is then put into the tube; the portion which adheres to the mortar can be completely removed by being rubbed with small quantities of the dry powder of chloride of sodium. The operator first places at the bottom of the tube, a mixture of chloride of sodium with a little chlorate of potash. The mixture is then introduced above. The last fourth part of the mixture is mixed with an additional quantity of chloride of sodium, in order that the decomposition may be more easily managed at the commencement of the operation. Above the mixture, a small quantity of chloride of sodium mixed with a little chlorate of potash, is placed. By putting chlorate of potash both before and after the substance which is to be decomposed, two very important objects are gained. In the first place, the operation commences with a disengagement of oxygen gas, so that the substance to be decomposed is already in an atmosphere of oxygen gas, at the moment when the heat begins to act upon it. And, secondly, when the decomposition is ended, the carbonic acid gas and aqueous vapour remaining in the tube and other parts of the apparatus are effectually driven forward to their proper places by the final current of oxygen gas. When the entire mixture has thus been placed in the tube, the upper part of the tube is drawn out over a lamp, and the point is bent at an obtuse angle.





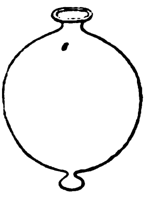
The contracted point of the tube is placed in a little vessel which serves as a receiver. This has the shape of the annexed figure, *c*, and must be as small as possible. This vessel is connected with the tube, *a*, in which the combustion is operated, by a tube of Indian rubber. The use of this receiver is to collect the water produced during the experiment. That none of the water may be lost, the gas which passes from the vessel *c* is led into a glass tube, *d*, filled with chloride of calcium and connected with the receiver, *c*, by a tube of Indian rubber. The other end of the tube, *d*, is connected by a tube of Indian rubber, with a gas-conducting tube leading to the mercurial trough. The following figure represents the whole apparatus. The receiver, the tube with the chloride of calcium, and the caoutchouc connectors, are all weighed before the experiment.



The pressure of the mercury in the trough upon the gas which is disengaged from the tube, sometimes causes the expansion of the tube while softened by the heat, to such a degree as to produce a hole. To prevent this, the tube is wrapped round very tight with thin tin plate, and is bound round with iron wire. The tube thus armed is heated in an oblong furnace, which can be set up with a few bricks. The heat is first applied to the upper part of the tube, and the lower part is protected from the heat by a moveable screen of iron plate, which is so contrived that the tube can pass through it. The screen is moved backwards in proportion as the combustion proceeds, while the upper part of the glass tube, where the combustion is ended, is kept in a constant state of ignition.

The quantity of the substance submitted to analysis must not be too great, when all the gas it produces is to be collected; five, or, at most, eight grains is the proper quantity. If the substance contains only hydrogen, carbon, and oxygen, then merely the quantity of the water and the carbonic acid gas is determined. The quantity of the water is ascertained by direct weighing. A little water always remains in the sharp point of the tube in which the combustion is effected. This point is therefore cut off with a file, and weighed with the receiver and the chloride of calcium tube. It is afterwards separated, dried, and weighed alone. The weight is deducted from the weight of the receiver and the tube weighed with it. What the latter then weigh more than they weighed before the experiment, is equal to the weight of the water.

The quantity of the resulting gas can be estimated either according to weight or to volume. In the first case, it is collected under a bell glass sufficiently large to receive all the gas disengaged during the experiment. The operator introduces, into this receiver, a little glass vessel, containing caustic potash, and bound over at the mouth with glove leather. This little vessel has the form of the annexed figure, *e*. After it has been weighed, it is fastened by means of the knob at the bottom to a fine ignited iron wire, by which it can be pushed through the mercury into the receiver, *f*. When the mercury ceases to ascend in the receiver, the whole is allowed to repose for twelve hours, the vessel *e* remaining in the receiver. At the end of that time, the vessel *e* is taken out, cleansed from adhering particles of mercury, and weighed. The increase of weight indicates the quantity of carbonic acid.



If, on the contrary, the gas is to be estimated according to volume, the operator must collect the gas in glass tubes of not too great a diameter. These tubes must be graduated, and it is always best when they are divided into cubic centimeters (see page 382). Several of these tubes should be in readiness, that the operator may be able to collect all the gas. They must be pressed into the mercury until the latter stands equally high both within and without the tube. The carbonic acid must then be absorbed, in the well known manner, by a piece of moistened potash. By this means, the operator finds the volume of the carbonic acid gas, from which he then calculates the quantity of carbon. This method, however, is subject to more accidents than the former. BERZELIUS, therefore, always employs the former method, when the substance submitted to analysis contains no nitrogen. When nitrogen forms a constituent of a substance thus examined, it is necessary, as will be described farther on, to adopt another course of procedure.

This method has the advantage of permitting the quantity of the hydrogen to be estimated with great accuracy, since the water afforded by the decomposition is collected and weighed. When, however, the substance submitted to analysis is not quite anhydrous, then the water obtained is partly that which was present in the compound, partly that produced by the hydrogen.

Employment of Oxide of Copper in the Analysis of Organic Substances.—Chlorate of potash cannot be employed with advantage in the analysis of substances which contain nitrogen. The excess of oxygen can easily produce nitric acid, and on employing a smaller quantity of chlorate of potash, the combustion is effected but imperfectly. GAY-LUSSAC has therefore recommended the deutoxide of copper to be employed in decompositions of this description. The superiority of deutoxide of copper over chlorate of potash is now so universally acknowledged, that it is almost invariably employed in organic analyses, even with substances which do not contain nitrogen. GAY-LUSSAC recommended at first, for the prevention of errors in the case of the production of nitric acid by substances containing nitrogen, the putting of metallic copper, in the state of filings or spirals of fine wire, into the tube above the oxide of copper, and considered that it would be proper to keep this metallic copper in a continual state of ignition during the experiment, in order that the oxides of nitrogen might be reduced. According to BERZELIUS, however, this precaution is quite unnecessary.

The apparatus employed in these experiments has often been so contrived, that the water produced by the decomposition could not be weighed. In such a case, the quantity of hydrogen contained in the substance submitted to analysis must be ascertained by calculation. It is then necessary to weigh the tube with the deutoxide of copper both before and after the experiment. The loss of weight, sustained in consequence of the ignition, indicates at once the quantity of the substance submitted to examination, and of the oxygen of which the deutoxide of copper has been deprived by the combustion. If the weight of the resulting gases is then determined, the difference between this weight and the loss of weight sustained by the tube, is the weight of the water produced.—According to **Berzelius**, however, it is extremely difficult to weigh the tube after the ignition with a proper degree of accuracy; because, as the experiment requires the employment of a red heat, it is necessary to envelope the tube in tin plate to prevent its expansion. If, with a view to avoid the use of the metallic envelope, a feebler heat were applied, the combustion, in a great number of cases, would be effected but imperfectly.

Attempts have been made to heat the glass tube by the flame of a spirit lamp. It is then much easier to weigh the tube after the experiment. But as it is absolutely essential, when the operation is nearly at an end, to ignite the whole of the glass tube at once; and as the management of a spirit lamp with a wick as long as the glass tube, is accompanied by difficulties, it is better to prefer the uniform heat afforded by a charcoal fire.

The deutoxide of copper employed in these experiments can be best prepared as follows: Copper is dissolved in pure nitric acid, the solution is evaporated to dryness, and the salt is strongly ignited in a platinum crucible. The resulting deutoxide of copper contains no traces of nitric acid, if the heat has been sufficiently powerful. It is much more difficult to prepare deutoxide of copper of equal purity by any other process.

A very disagreeable circumstance attending the employment of the deutoxide of copper is, that it has the property of absorbing hygrometric moisture with greater readiness than most other pulverulent substances. It is, consequently, necessary to ignite the deutoxide of copper immediately before the experiment, to weigh it while hot, and to mix it as rapidly as possible, and in a hot mortar, with the substance which is to be analysed. By proceeding thus, the absorption of moisture can be almost entirely avoided. **Berzelius** has succeeded in analysing substances which were free from hydrogen, and in experiments which required from 400 to 600 grains of deutoxide of copper, without obtaining more than the sixtieth part of a grain of water.

Gay-Lussac and **Liebig** (*Annales de Chimie et de Physique*, T. xxv. p. 290) recommend the following method of expelling hygrometric moisture from the mixture of the substance for analysis with the deutoxide of copper: The glass tube in which the mixture has been placed, is connected with a tube filled with chloride of calcium. The latter is connected by a flexible tube of lead, with a glass receiver standing on the table of an air-pump. When the apparatus is exhausted of air by the pump, the moisture passes out of the tube with the air. When air is allowed to enter the apparatus, it must pass necessarily through the tube containing the chloride of calcium, and become perfectly dry before it enters the tube containing the mixture. But, in order still more effectually to drive the hygrometric water from the mixture, it is good to immerse the glass tube which contains the mixture in another tube of very large diameter and full of water kept boiling hot. The large glass tube must be closed by a cork having two holes bored through it; the glass tube with the mixture is put through one of these holes, and a bent tube to carry off the steam through the other. If, now, the operator alternately exhausts the apparatus of air, and allows fresh air to enter the tube through the chloride of calcium, the mixture is naturally deprived of its hygrometric water.

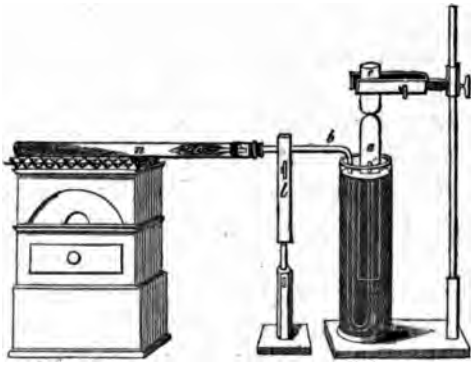
When the combustion of the substance is completed, there always remains a small quantity of the gaseous product, both in the tube and the receiver. That this may lead to the smallest possible error, these parts of the apparatus are made extremely small: the tube which leads from the apparatus to the mercurial trough must only be a large thermometer tube. Yet, this loss can, according to BERZELIUS, be altogether avoided, by proceeding as follows: The operator mixes a few grains of fused chlorate of potash with three or four times as much deutoxide of copper. He places this mixture at the bottom of the tube, puts above it as much pure deutoxide of copper as occupies an inch of the length of the tube, and then introduces the mixture which is to be analysed. When the ignition of the substance is finished, and the disengagement of gas ceases, then heat is applied to the extreme end of the tube, to cause the decomposition of the chlorate of potash. The oxygen gas which then escapes, drives all the other gas out of the apparatus, and carries it into the bell-glass of the mercurial trough.

This method can be extremely well employed in the analysis of the substances which contain no nitrogen, and in which case all the gas can be collected in one receiver. But, in the analysis of the substances which contain nitrogen, it is necessary to collect the disengaged gas in at least three different glass tubes. The gas in the first tube then contains the small quantity of atmospheric air which remained in the apparatus at the commencement of the operation; *that* in the second tube is entirely free from impurities; *that* in the third tube contains the oxygen gas expelled from the chlorate of potash. The volume of the carbonic acid gas contained in the three glass tubes must be accurately determined in the usual manner, by caustic potash. The operator must determine with great accuracy the relation in volume of the carbonic acid to the nitrogen gas in the second tube. According to the relation so determined, the quantity of nitrogen gas contained in the other tubes, can be calculated from the quantity of carbonic acid gas found there; for, the relative proportions of the two gases are in all cases the same.

PELLETIER et DUMAS (*Annales de Chimie et de Physique*, T. XXIV. p. 165) employed two equal portions of the substance for analysis; each portion was mixed with the proper quantity of deutoxide of copper, and both portions were placed in one tube, but separated from one another by such a quantity of powdered glass, that while the ignition of one portion took place, the other portion remained unaffected. During the ignition of the first portion, they collected nothing but the water, and allowed the gases to escape. This had the effect of completely carrying the atmospheric air out of the apparatus. Then the second portion was decomposed, and both the water and the gases were collected. They thus obtained the gases free from impurities; but they obtained, at the same time, twice as much water as belonged to the quantity of gas obtained.

GAY-LUSSAC and LIEBIG (*Annales de Chimie et de Physique*, T. XXV. p. 301) have employed another method in the analysis of substances which contain nitrogen. The object of this method was to collect the disengaged gases free from the least mixture of atmospheric air, and to effect the determination of the relative proportions of carbonic acid gas and nitrogen gas with the greatest possible accuracy. To the glass tube which contained the mixture of the substance for analysis with deutoxide of copper, they joined a copper tube, and to the latter a glass tube to receive the gases resulting from the decomposition. This glass tube was bent at a right angle, and the perpendicular descending branch, which was 39 inches long, dipped into a vessel of mercury. With the copper tube, there was another connected at a right angle. This was provided with a stop-cock, and placed in connection with an air-pump by means of a flexible tube of lead. Upon exhausting the apparatus of air, the mercury rose in the long glass tube to the height of about 30 inches. When the mercury had risen as high as it could rise, the stop-cock was shut, and the connection with the air-pump entirely cut off. The mixture being then ignited, the disengaged gases were obtained quite free from atmospheric air. The relative proportions of the different gases in the gaseous mixture could then be determined with great accuracy.—It is of particular importance, in the analysis of compounds containing cyanogen, to determine the relative proportions of the gases produced. The gaseous mixture produced by the ignition of the cyanurets with deutoxide of copper, must contain precisely two volumes of carbonic acid to one volume of nitrogen.

The apparatus employed by GAY-LUSSAC and LIEBIG, in the analysis of substances by means of deutoxide of copper, is somewhat different from that employed by BERZELIUS. It is represented below. The graduated glass tube *a*, which is intended to receive the gases, is placed in a glass vessel. The tube *b* which is to conduct the gas into the graduated tube has two parallel perpendicular arms, of which the one which rises is sufficiently long nearly to touch the top of the graduated tube, when the latter is forced down as far as it can go; the other arm of the conducting tube rises up on the other side of the graduated tube. When the large glass vessel has been filled with mercury, and the end of the conducting tube has been placed within the graduated tube, the latter is pressed down into the mercury; the atmospheric air is thus driven out through the conducting tube. The graduated tube is



fastened in its new situation by being pressed between the cheeks of a holdfast which can be raised on a staff to any given height, and then be secured by a screw; or it is secured in the manner represented in the above figure, namely, by the cork *e*, which is fastened in the holdfast. When the apparatus is thus prepared, the tube *n* which contains the mixture of the substance for examination with deutoxide of copper, is connected with the conducting tube *b*, and the latter is secured in its place by being pressed between the cheeks of the holdfast *l*. The mercury in the graduated tube *a*, is now brought to the same level with the mercury in the large glass, and the volume of the atmospheric air which remains in the graduated tube is accurately measured. As soon as the substance begins to be decomposed by the heat, the disengaged gas presses down the mercury in the graduated tube. It is, therefore, necessary to raise the graduated tube out of the glass vessel, by screwing the arm of the holdfast higher and higher, as fast as the gas comes over. When the decomposition is at an end, the fire is removed, and the whole is allowed to cool. The mercury within the graduated tube is then brought on a level with that on the outside. It is evident, that the volume of gas which has passed into the graduated tube during the operation, is precisely equal to the whole quantity of gas produced by the decomposition. The estimation of the water is effected by GAY-LUSSAC and LIEBIG as follows: They place the tube *o*, containing the chloride of calcium which is to absorb the water, within the tube containing the mixture. The tube containing the chloride of calcium fits the large tube exactly, and is drawn out to a point at the end which is turned towards the mixture to be decomposed. It is weighed before it is put in its place. The tube containing the mixture is then closed by a cork, through which the conducting tube passes. The juncture must be air-tight. The tube, without being previously enveloped, is then laid on a grate of iron wire supported by a furnace, the door and ash-hole of which are closed. It is then brought to ignition by the application of red-hot charcoal.

TH. VON SAUSSURE, in analysing substances which were free from nitrogen, employed oxygen gas, instead of chlorate of potash or deutoxide of copper. Since oxygen gas does not change its volume when converted into carbonic acid gas, it is possible, from the diminution of volume occasioned by the combustion, to estimate the quantity of hydrogen contained in the substance analysed.—PROUT (Philosophical Transactions, 1827, Part II. p. 355) employed an apparatus of a different description in this kind of analysis. He ignited the substances for examination with deutoxide of copper, in an instrument which contained a determinate quantity of oxygen gas. After the combustion was ended, he led the oxygen gas backwards and forwards over the deutoxide of copper, with a view to reconvert all the reduced copper into deutoxide of copper. If the substance submitted to analysis according to this method, contain oxygen and hydrogen in the proportions necessary to constitute water, then the volume of the oxygen gas employed remains unchanged. If it contain oxygen in excess, the volume of the oxygen gas is increased. If it contain hydrogen in excess, the volume of the oxygen gas is diminished. The apparatus appears, however, to be too complicated to give such accurate results as the apparatus of BERZELIUS. The circumstantial description of it may, therefore, be omitted.

Method of Operating with Liquids.—When the substance which is to be decomposed by deutoxide of copper, can be obtained only in the liquid state, it is best to proceed as follows: A very small oblong glass bulb with a very fine point is prepared. This is weighed, and then filled with the liquid for examination. The way to introduce the liquid is, to warm the glass bulb, and to plunge the point into the liquid; then, as the bulb becomes cool, the liquid rises into it, in consequence of the pressure of the atmosphere. The bulb is then weighed with the liquid. The operator places the bulb at the bottom of a long glass tube, and fills the latter completely with deutoxide of copper. He then connects the tube with an apparatus proper to collect the water and gases which may be produced. Heat is first applied to that portion of the deutoxide of copper which is farthest from the substance for examination. When the deutoxide of copper is red-hot at that end, the other part is warmed extremely feebly. A very small quantity of the substance escapes from the point of the glass bulb, and traverses the red-hot deutoxide of copper. It is, of course, immediately decomposed. After some time, the heat is rendered so powerful as to ignite the whole tube.—It will be readily understood, that if the vaporised substance passes too quickly through the red-hot deutoxide of copper, a considerable quantity of it can escape decomposition.

Decomposition of Gases by Deutoxide of Copper.—The deutoxide of copper can also be employed in the quantitative examination of several gaseous compounds of hydrogen. The different gaseous compounds of hydrogen and carbon, for example, can be thus analysed. A considerable excess of deutoxide of copper is placed in a porcelain tube, and heated to redness. An indefinite quantity of the gas to be analysed is then passed very slowly over the ignited deutoxide of copper. It is unnecessary to collect the water and carbonic acid gas which are produced at first; it is better, on the contrary, to wait till all the atmospheric air has been expelled from the apparatus. The operator then collects, and determines the relative quantities of the water and gaseous carbonic acid produced.

Precautions to be taken to ensure Accuracy in Organic Analyses.—The analysis of what are commonly termed organic substances, which are compounds that consist of hydrogen, carbon, oxygen, with sometimes a portion of nitrogen, if executed in the manner which has been described above, is still of no value, unless the substance submitted to examination is, in every case, perfectly pure, and free from all extraneous matters. These are conditions, however, which it is very difficult to fulfil, especially when the substance to be analysed is one that cannot be obtained in the state of crystals. If the substance be capable of producing saline compounds by combining with bases, it is proper to determine with accuracy the saturating capacity of the substance. The saturating capacity of a substance is ascertained, according to BERZELIUS, in the easiest and most certain manner, by combining the substance with protoxide of lead and determining the composition of the resulting compound. It is hereby particularly necessary to take care not to employ mixtures of different compounds, or differently saturated compounds. The compound is dried with all possible accuracy. It is then laid on a small thin capsule of glass, which is first weighed alone and again with the substance upon it. The capsule is then heated over a spirit lamp till the mass takes fire at the edges: in most cases, the lamp may then be removed, because the combustion spreads to all parts of the mass. When the combustion ceases, the capsule is again heated by the spirit lamp, but it is proper to avoid too strong a heat. When the capsule is cold, it is weighed with its contents. The residue is a mixture of protoxide of lead with metallic lead. The weighed mass is treated with acetic acid, which dissolves the protoxide of lead, but is without action on the metallic lead. The latter is then washed with water. The edulcoration can be very well effected without occasioning any loss of lead. The lead is then dried and weighed on the capsule. By this method of proceeding the operator learns how much protoxide of lead has been dissolved by the acetic acid. He then calculates how much protoxide of lead could be produced by the combination with oxygen of the metallic lead afforded by the experiment. He thus learns the weight of the whole quantity of protoxide of lead combined with the organic substance submitted to investigation. The saturating capacity of the substance can then be easily calculated. This experiment, which requires, however, to be several times repeated, affords, with proper care, a much more accurate result than can be obtained by attempting to determine the proportion of protoxide of lead contained in the compound by any other process.

Suppose, now, that a weighed quantity of such an organic substance has been decomposed by means of deutoxide of copper, and that the respective proportions of hydrogen and carbon have been experimentally ascertained, and the quantity of the oxygen has been calculated from the loss. The substance may be analysed alone, but it is as good or better to analyse a compound of the substance with a base, such as protoxide of lead, but not with an alcali or alcaline earth, since the latter retain carbonic acid. In making a calculation of the results, the operator must first examine whether the quantity of oxygen afforded by the analysis is a multiple, by a whole number, of the saturating capacity of the substance determined by the previous experiment; the quantity of the oxygen must, at any rate, deviate in a very inconsiderable degree from a multiple of the number which expresses the said saturating capacity. For, as in the case of the salts formed by the inorganic acids with bases, the oxygen of the former must be a multiple by a whole number of the oxygen of the latter, so must this be also the case with the compounds of organic substances with bases. When, therefore, this relation between the oxygen and the saturating capacity of the compound is not found to exist, the inference to be drawn is, either that the analysis is incorrect, or that the substance submitted to analysis was not in a state of purity.—The number of atoms of hydrogen, carbon, and oxygen contained in the substance submitted to examination can now be easily reckoned. If it be supposed that the substance contains exactly so many more times the number of atoms of oxygen than are contained in the base with which it forms a neutral compound, as the number expressing the quantity of oxygen in the substance is greater than that expressing the quantity of oxygen in the base, then it is easy to ascertain the number of the atoms of hydrogen, carbon, and nitrogen, if the latter be a constituent of the substance.

It is much more difficult to judge of the accuracy of such an analysis, when the organic substance which has been decomposed is one which forms no saline compounds with bases. In cases of this description, the operator must be satisfied with examining whether the relative proportions of the constituents, as made known by the analysis, are equivalent to numbers expressing whole atoms of carbon, hydrogen, oxygen, and nitrogen. This correspondence, however, can very easily take place with very slight deviations from the proper proportions, when the substance experimented upon is composed of a great number of atoms of the four elementary bodies, and yet the analysis affording these corresponding numbers may be quite false.

INDEX.

ALUMINUM. Detection of Alumina in simple soluble compounds, i. 8—in simple insoluble compounds, 15—in complex soluble compounds, 26—in complex insoluble compounds, 36.—Behaviour of Alumina towards reagents, 74.

Quantitative estimation of Alumina, ii. 30.—Separation of Alumina from Magnesia, 31—from Lime, 34 and 36—from Strontian, 35—from Barytes, 36—from the Alcalies, 36—from Glucina, 37—from Yttria, 39—from the oxides of Cerium, 40—from Zirconia, 41—from protoxide of Manganese, 46—from peroxide of Iron, 60—from oxide of Zinc, 80—from oxide of Cobalt, 89—from oxide of Nickel, 96—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 108—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Tin, 164—from the oxides of Antimony, 180—from Chromic acid and the oxide of Chromium, 193—from Arsenious acid and Arsenic Acid, 202 and 204—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from Phosphoric acid, 256—from Silicic acid, 273, 283, 287.

ANTIMONY. The quantitative estimation of Antimony in its compounds is effected, in many cases, like that of the protoxide of Antimony.—Separation of Antimony from Nickel, ii. 181, 183—from Cobalt, 181, 183—from Zinc, 181—from Iron, 181—from Manganese, 181—from Mercury, 181—from Silver, 181, 183, 185—from Copper, 181, 183—from Bismuth, 181—from Lead, 181, 183—from Cadmium, 181—from Gold, 183—from Platinum, 183—from Tin, 185—from Arsenic, 207—from Tellurium, 214—from Selenium, 222—from Sulphur, 228, 236, 238, 241—from Chlorine, 349, 354.

Detection of protoxide of Antimony in simple soluble compounds, i. 8—in simple insoluble compounds, 13—in complex soluble compounds, 22—in complex insoluble compounds, 35. —Behaviour of protoxide of Antimony towards reagents, 147.—Quantitative estimation of protoxide of Antimony, ii. 174.—Separation of protoxide of Antimony from the Alcalies, 180—from the Earths, 180—from oxide of Nickel, 181—from oxide of Cobalt, 181—from oxide of Zinc, 181—from peroxide of Iron, 181—from protoxide of Manganese, 181—from oxide of Cadmium, 181—from protoxide of Lead, 181—from oxide of Bismuth, 181—from deutoxide of Copper, 181—from oxide of Silver, 181—from peroxide of Mercury, 181—from Antimonious acid and Antimonic acid, 187—from Arsenious acid and Arsenic acid, 207—from Sulphuric acid, 243—from Phosphoric acid, 251.

Quantitative estimation of Antimonious acid and Antimonic acid, ii. 174.—The separation of these acids from other substances is the same as the separation of protoxide of Antimony from the same.

ARSENIC. The quantitative estimation of Arsenic is mostly the same as that of Arsenious acid and Arsenic acid.—Separation of Arsenic from Nickel, ii. 202—from Cobalt, 202 and 203—from Zinc, 202 and 203—from Iron, 202 and 203—from Manganese, 202 and 203—from Cadmium, 203—from Lead, 203—from Antimony, 207—from Tellurium, 214—from Selenium, 222—from Sulphur, 237, 239—from Chlorine, 349, 352—from Hydrogen, 415.

Behaviour of Arsenious acid towards reagents, i. 193.—Quantitative estimation of Arsenious acid, ii. 198.—Separation of Arsenious acid from the Alcalies, 202 and 204—from the Earths, 202 and 204—from protoxide of Manganese, 202 and 203—from peroxide of Iron, 202 and 203—from oxide of Zinc, 202 and 203—from oxide of Cobalt, 202 and 203—from oxide of Nickel, 202—from the oxides of Uranium, 202—from Titanic acid, 202—From Chromic acid and the oxide of Chromium, 202—from oxide of Cadmium, 203—from protoxide of Lead, 203—from oxide of Bismuth, 203—from deutoxide of Copper, 203—from oxide of Silver, 203—from peroxide of Mercury, 203 —from peroxide of Tin, 207—from the oxides of Antimony, 207—from Arsenic acid, 211—from oxide of Tellurium, 214—from Selenic acid, 222—from Sulphuric acid, 243—from Phosphoric acid, 251.

Detection of Arsenic acid in simple soluble compounds, i. 11

—in simple insoluble compounds, 13, 18, 19—in complex soluble compounds, 31—in complex insoluble compounds, 35, 44.—Behaviour of Arsenic acid towards reagents, 191.—Quantitative estimation of Arsenic acid, ii. 198.—The separation of Arsenic acid from other substances is mostly the same as that of Arsenious acid from the same.—Separation of Arsenic acid from Barytes, Strontian, Lime, and protoxide of Lead, 205—from Arsenious acid, 211—from Chlorides, 361.

BARIUM. Separation of Barium from Sulphur, ii. 228—from Chlorine, 349.

Detection of Barytes in simple soluble compounds, i. 9—in simple insoluble compounds, 15, 16, and 20—in complex soluble compounds, 28—in complex insoluble compounds, 36 and 44.—Behaviour of Barytes towards reagents, 60.

Quantitative estimation of Barytes, ii. 12.—Separation of Barytes from the Alcalies, 13—from Strontian, 14—from Lime, 19—from Magnesia, 28—from Alumina, 36—from Glucina, 39—from Yttria, 39—from the oxides of Cerium, 40—from Zirconia, 41—from protoxide of Manganese, 51—from peroxide of Iron, 61—from oxide of Zinc, 81—from oxide of Cobalt, 90—from oxide of Nickel, 97—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 108—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Tin, 164—from Titanic acid, 173—from the oxides of Antimony, 180—from Chromic acid and the oxide of Chromium, 193—from Arsenious acid and Arsenic acid, 202, 204, and 205—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from the other acids of Sulphur, 246—from Phosphoric acid, 258—from Phosphorous acid and Hypophosphorous acid, 265—from Oxalic acid, 320—from Carbonic acid, 325—from Boracic acid, 329—from Nitric acid, 373.

BISMUTH. The quantitative estimation of Bismuth is mostly like that of oxide of Bismuth.—Separation of Bismuth from Sulphur, ii. 226, 241.

Detection of oxide of Bismuth in simple soluble compounds, i. 6—in simple insoluble compounds, 13—in complex soluble compounds, 22—in complex insoluble compounds, 36—Behaviour of oxide of Bismuth towards reagents, 114.

Quantitative estimation of oxide of Bismuth, ii. 103.—Separation of oxide of Bismuth from protoxide of Lead, 104—from oxide of Nickel, 105—from oxide of Cadmium, 105—from oxide of Cobalt, 105—from oxide of Zinc, 105—from peroxide of Iron, 105—from protoxide of Manganese, 105—from the Earths, 105 from the Alcalies, 105—from the oxides of Uranium, 107—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 129—from the oxides of Tin, 164—from Titanic acid, 169—from the oxides of Antimony, 181—from Chromic acid and the oxide of Chromium, 196—from Arsenious acid and Arsenic acid, 203—from oxide of Tellurium, 213—from Selenious acid, 217—from Sulphuric acid, 243—from Phosphoric acid, 251 and 253—from Carbonic acid, 321—from Nitric acid, 372.

BORON. Separation of Boron from Fluorine, ii. 335.

Detection of Boracic acid in simple soluble compounds, i. 11. in simple insoluble compounds, 18—in complex soluble compounds, 31—in complex insoluble compounds, 39.—Behaviour of Boracic acid towards reagents, 176.

Quantitative estimation of Boracic acid, ii. 328.—Separation of Boracic acid from various metallic oxides, 329—from Barytes, 329—from Strontian, 329—from Lime, 329—from protoxide of Lead, 329—from all other fixed Bases, 329—from Silicic acid, 330.

BROMINE. Behaviour of metallic Bromides towards reagents, i. 195.—Quantitative estimation of Bromine in its compounds, ii. 365.—Separation of Bromine from Chlorine, 367—from Iodine, 368—from Hydrogen, 407.

Behaviour of Bromic acid towards reagents, i. 165.

CADMIUM. The quantitative estimation of Cadmium in its compounds is the same as that of oxide of Cadmium.—Separation of Cadmium from Sulphur, ii. 223.

Detection of oxide of Cadmium in simple soluble compounds, i. 7—in simple insoluble compounds, 13—in complex soluble compounds, 22—in complex insoluble compounds, 35.—Behaviour of oxide of Cadmium towards reagents, 107.

Quantitative estimation of oxide of Cadmium, ii. 97.—Separation of oxide of Cadmium from oxide of Nickel, 97—from oxide of Cobalt, 97—from oxide of Zinc, 97—from peroxide of Iron, 97

—from protoxide of Manganese, 97—from the Earths, 97—from the Alcalies, 97—from protoxide of Lead, 103—from oxide of Bismuth, 105—from the oxides of Uranium, 107—from deutoxide of Copper, 114—from oxide of Silver, 116—from peroxide of Mercury, 129—from the oxides of Tin, 164—from Titanic acid, 169—from the oxides of Antimony, 181—from Chromic acid and the oxide of Chromium, 196—from Arsenious acid and Arsenic acid, 203—from oxide of Tellurium, 213—from Selenious acid, 217—from Selenic acid, 219—from Sulphuric acid, 243—from Phosphoric acid, 251 and 253—from Carbonic acid, 321.

CALCIUM. Detection of Lime in simple soluble compounds, i. 9—in simple insoluble compounds, 15, 16, and 20—in complex soluble compounds, 28—in complex insoluble compounds, 36 and 44.—Behaviour of Lime towards reagents, 66.

Quantitative estimation of Lime, ii. 16.—Separation of Lime from Strontian, 18—from Barytes, 19—from the Alcalies, 22—from Magnesia, 26—from Alumina, 34—from Glucina, 39—from Yttria, 39—from the oxides of Cerium, 40—from Zirconia, 41—from protoxide of Manganese, 48—from peroxide of Iron, 61—from oxide of Zinc, 81—from oxide of Cobalt, 89—from oxide of Nickel, 96—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 108—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Tin, 164—from Titanic acid, 172—from the oxides of Antimony, 180—from Tungstic acid, 188—from Molybdic acid, 190—from Chromic acid and the Oxide of Chromium, 193—from Arsenious acid and Arsenic acid, 202, 204, and 205—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from the other acids of Sulphur, 246—from Phosphoric acid, 258—from Phosphorous acid and Hypophosphorous acid, 265—from Silicic acid, 273, 283, 288—from Oxalic acid, 320—from Carbonic acid, 325—from Boracic acid, 329—from Chlorous acid, 363.

CARBON. Quantitative estimation of Carbon, ii. 306.—Separation of Carbon from Silicates, 308—from Sulphur, 309—from Sulphur and Saltpetre: analysis of Gunpowder, 311—from Iron, 312—from Chlorine, 359—from Nitrogen: method of analysing Cyanurets, 376—from Hydrogen, 407.—Separation of the gaseous compounds of Carbon and Hydrogen from one another, 407—from other gases, 410.—Analysis of all compounds of Carbon and Hydrogen, 412.—Analysis of Carbonaceous substances by means of Chlorate of Potash, 415—by means of oxide of Copper, 420.

Quantitative estimation of Carbonic oxide gas, ii. 318.—Separation of Carbonic oxide gas from Carburetted hydrogen gas, 410.

Quantitative estimation of Oxalic acid, 319—of the soluble Oxalates, 320—of the insoluble Oxalates, 320.

Detection of Carbonic acid in simple soluble compounds, i. 10—in simple insoluble compounds, 17—in complex soluble compounds, 31—in complex insoluble compounds, 38.—Behaviour of Carbonic acid towards reagents, 178.

Quantitative estimation of Carbonic acid in a gaseous state, ii. 321.—Quantitative estimation of Carbonic acid in fixed substances, 321.—Separation of Carbonic acid from protoxide of Lead, 322—from oxide of Cadmium, 322—from protoxide of Iron, 322—from protoxide of Manganese, 322—from oxide of Cobalt, 322—from Water, 323—from the Alcalies, 325—from Barytes, 325—from Strontian, 325—from Lime, 325—from Chlorides, 361—from Carburetted hydrogen gas, 410—from Atmospheric air, 412.

CERIUM. Behaviour of the oxides of Cerium towards reagents, i. 82.

Quantitative estimation of the oxides of Cerium, ii. 39.—Separation of the oxides of Cerium from Yttria, 40—from Glucina, 40—from Alumina, 40—from Magnesia, 40—from Lime, 40—from Strontian, 40—from Barytes, 40—from the Alcalies, 40—from Zirconia, 41—from protoxide of Manganese, 45—from peroxide of Iron, 59—from oxide of Zinc, 80—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Tin, 164—from Titanic acid, 172—from Sulphuric acid, 243.

CHLORINE. Detection of Chlorine in simple soluble compounds, i. 12—in simple insoluble compounds, 18, 20—in complex soluble compounds, 33—in complex insoluble compounds, 39, 43.—Behaviour of Metallic Chlorides towards reagents, 194.

Quantitative estimation of Chlorine in its compounds, ii. 349.—Separation of Chlorine from Phosphorus, 349 and 352—from Sulphur, 349 and 355—from Selenium, 349, 352, and 354—from Arsenic, 349, 352—from Chromium, 349—from Titanium, 349, 353—from Tin, 349, 352—from Antimony, 349, 354—from Silver, 356—from Mercury, 357—from various Metals, 358—from Manganese, 359—from Iron, 359—from Zinc, 359—from Cobalt, 359—from Carbon, 359—from Carbonates, 361—from Silicates, 360—from Fluorides, 361—from Arseniates, 361—from Phosphates, 361—from Chlorates, 365—from Bromine, 367—from Iodine, 368—from Nitrogen, 376—from Hydrogen, 407.

Quantitative estimation of Chlorine gas, ii. 361.—Separation of Chlorine gas from other gases, 411.

Quantitative estimation of Chlorous acid and the Chlorites (or Chlorides of Earths and Alcalies), ii. 363.

Behaviour of Chloric acid towards reagents, i. 163.—Quantitative estimation of Chloric acid and the Chlorates, ii. 362.—Separation of Chlorates from Chlorides, 365.

CHROMIUM. Behaviour of oxide of Chromium towards reagents, i. 149.—Quantitative estimation of oxide of Chromium, ii. 191. —Separation of oxide of Chromium from the Alcalies, 193—from the alcaline Earths, 193—from Magnesia, 193—from Alumina, 193—from protoxide of Manganese, 193—from oxide of Zinc, 193—from oxide of Cobalt, 193—from oxide of Nickel, 193—from peroxide of Iron, 193—from protoxide of Iron, 193 —from protoxide of Lead, 196—from deutoxide of Copper, 196 —from oxide of Silver, 196—from Chromic acid, 197—from Arsenious and Arsenic acid, 202—from Sulphuric acid, 243 and 245—from Phosphoric acid, 254—from Silicic acid, 297.

Behaviour of Chromic acid towards reagents, i. 190.—Quantitative estimation of Chromic acid, ii. 191.—Separation of Chromic acid from oxide of Chromium, 197.—The separation from other substances is effected like that of oxide of Chromium from the same.

COBALT. The quantitative estimation of Cobalt in its compounds is the same as that of oxide of Cobalt.—Separation of Cobalt from Sulphur, ii. 223—from Phosphorus, 255—from Chlorine, 359.

Detection of oxide of Cobalt in simple soluble compounds, i. 8—in simple insoluble compounds, 14—in complex soluble compounds, 26—in complex insoluble compounds, 36.—Behaviour of oxide of Cobalt towards reagents, 96.

Quantitative estimation of the oxide of Cobalt, ii. 82.—Separation of oxide of Cobalt from oxide of Zinc, 85—from peroxide of Iron, 86—from protoxide of Manganese, 87—from Alumina, 89—from Magnesia, 89—from Lime, 89—from Strontian, 90—from Barytes, 90—from the Alcalies, 90—from oxide of Nickel, 92—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 107—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Tin, 164—from Titanic acid, 169—from the oxides of Antimony, 181 and 183—from Chromic acid and the oxide of Chromium, 196—from Arsenious and Arsenic acids, 202 and 203—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from Phosphoric acid, 253—from Carbonic acid, 322—from Nitric acid, 373.

Behaviour of peroxide of Cobalt towards reagents, i. 99.

COPPER. The quantitative estimation of Copper in its compounds is mostly the same as that of deutoxide of Copper.—Separation of Copper from Silver, ii. 117—from Mercury, 122—from Gold, 159—from Tin, 164—from Antimony, 181 and 183—from Arsenic, 203—from Tellurium, 213—from Selenium, 217 and 220—from Sulphur, 223, 235—from Phosphorus, 255.

Detection of deutoxide of Copper in simple soluble compounds, i. 6—in simple insoluble compounds, 13—in complex soluble compounds, 22—in complex insoluble compounds, 36.—Behaviour of deutoxide of Copper towards reagents, 116.

Quantitative estimation of deutoxide of Copper, ii. 109.—Separation of deutoxide of Copper from the oxides of Uranium, 113—from oxide of Nickel, 113—from oxide of Cobalt, 113—from oxide of Zinc, 113—from peroxide of Iron, 113—from protoxide of Manganese, 113—from the Earths, 113—from the Alcalies, 113—from oxide of Bismuth, 113—from protoxide of Lead, 113—from oxide of Cadmium, 114—from oxide of Silver, 116—from peroxide of Mercury, 125—from peroxide of Rhodium, 133—from peroxide of Palladium, 135—from oxide of Platinum, 146—from oxide of Gold, 159—from the oxides of Tin, 164—from Titanic acid, 169—from the oxides of Antimony, 181, 183—from Chromic acid and oxide of Chromium, 196—from Arsenious acid and Arsenic acid, 203—from oxide of Tellurium, 213—from Selenious acid and Selenic acid, 217—from Sulphuric acid, 243—from Phosphoric acid, 251 and 253—from Silicic acid, 301—from Carbonic acid, 321—from Boracic acid, 329—from Nitric acid, 371.

FLUORINE. Detection of Fluorine in simple soluble compounds, i. 11—in simple insoluble compounds, 18—in complex soluble compounds, 31—in complex insoluble compounds, 39. —Behaviour of Metallic Fluorides towards reagents, 199.

Quantitative estimation of Fluorine in Fluorides, ii. 333.—Estimation of the Water contained in Fluorides, 333.—Separation of Fluorides from Hydrofluoric acid, 334.—Separation of Fluorine from Boron, 335—from Silicium, 336.—Separation of metallic Fluorides from Fluoride of Silicium, 338—Separation of Fluorides from Silicates, 340—from Phosphates, 346—from Sulphates, 348—from Chlorides, 361.

GLUCINUM. Behaviour of Glucina towards reagents, i. 77.—Quantitative estimation of Glucina, ii. 37.—Separation of Glucina from Alumina, 37—from Magnesia, 38—from Lime, 39—from Strontian, 39—from Barytes, 39—from the Alcalies, 39—from Yttria, 39—from the oxides of Cerium, 40—from Zirconia, 41—from protoxide of Manganese, 45—from peroxide of Iron, 60—from oxide of Zinc, 80—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Antimony, 180—from Arsenious acid and Arsenic acid, 202, 204—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243.

GOLD. Detection of Gold in simple soluble compounds, i. 6—in simple insoluble compounds, 13—in complex soluble compounds, 22—in complex insoluble compounds, 35.—Behaviour of the oxides and chlorides of Gold towards reagents, 139.

Quantitative estimation of Gold, ii. 157.—Separation of Gold from Silver, 159—from oxidable Metals, 159—from Platinum, 161—from Tin, 164—from Antimony, 183—from Arsenic, 206—from Tellurium, 214—from Selenium, 220—from Sulphur, 227.

HYDROGEN. Quantitative estimation of Hydrogen gas, ii. 381. —Separation of Hydrogen gas from Oxygen gas, 381—from Nitrogen gas, 390—from Oxygen gas and Nitrogen gas, 392.—Separation of Hydrogen from Chlorine, 407—from Bromine, 407—from Iodine, 407—from Cyanogen, 407—from Carbon, 407—from Phosphorus, 412—from Sulphur, 413—from Selenium, 415—from Tellurium, 415—from Arsenic, 415.—Analysis of substances which contain Hydrogen, by means of chlorate of Potash, 415—by means of deutoxide of Copper, 420.

Quantitative estimation of Water, ii. 393—in Salts, which are oxidised by heat, 394—in salts, which attract Carbonic acid from the air, 394.—Estimation of the water of crystallisation in Salts, 393—of Water mechanically enclosed, 395—in Salts, which are decomposed by heat, 396—in Acids, 398—in Bases, 400.

Detection of Ammonia in simple soluble compounds, i. 10—in complex soluble compounds, 30.—Behaviour of Ammonia towards reagents, 57.—Quantitative estimation of Ammonia in ammoniacal salts, ii. 400.—Estimation of Water in ammoniacal salts, 401.—Quantitative estimation of Ammonia in the gaseous state, 404.—Separation of Ammoniacal gas from other gases, 406.

IODINE. Behaviour of Metallic Iodides towards reagents, i. 197.

Quantitative estimation of Iodine in its compounds, ii. 367.—Separation of Iodine from Bromine, 368—from Chlorine, 368—from Nitrogen, 376—from Hydrogen, 407.

Behaviour of Iodic acid towards reagents, i. 167.

IRIDIUM. Quantitative estimation of Iridium, ii. 136.—Separation of Iridium from many other metals, 137—from Osmium, 139—from Platinum, Rhodium, and Palladium, 147 and 153.

IRON. Quantitative estimation of Iron, ii. 51.—Separation of Iron from Tin, 164—from Antimony, 180 and 181—from Arsenic, 202—from Tellurium, 213—from Selenium, 217—from Sulphur, 223, 237, 315—from Phosphorus, 255, 316—from Carbon, 312, 314—from Chromium, 317—from Chlorine, 359—from Silicium, 317—from Manganese, 318—from Titanium, 318.—Its separation from other substances is the same as the separation of peroxide of Iron from those substances.

Detection of protoxide of Iron in simple soluble compounds, i. 8—in simple insoluble compounds, 14—in complex soluble compounds, 26—in complex insoluble compounds, 36.—Behaviour of protoxide of Iron towards reagents, 102.—Quantitative estimation of protoxide of Iron, ii. 51.—Its separation from other substances is the same as the separation of peroxide of Iron from other substances, excepting the separation from peroxide of Iron, 63—from Carbonic acid, 322.

Detection of peroxide of Iron in simple soluble compounds, i. 7—in simple insoluble compounds, 13—in complex soluble compounds, 22, 26—in complex insoluble compounds, 36.—Behaviour of peroxide of Iron towards reagents, 104.—Quantitative estimation of peroxide of Iron, ii. 51.—Separation of peroxide of Iron from protoxide of Manganese, 53—from Zirconia, 58—from the oxides of Cerium, 59—from Yttria, 59—from Glucina, 60—from Alumina, 60—from Magnesia, 61—from Lime, 61—from Strontian, 61—from Barytes, 61—from the Alcalies, 61—from protoxide of Iron, 63—from oxide of Zinc, 75—from oxide of Cobalt, 86—from oxide of Nickel, 95—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 108—from deutoxide of Copper, 112, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from peroxide of Rhodium, 133—from oxide of Platinum, 146—from peroxide of Gold, 161—from the oxides of Tin, 164—from Titanic acid, 170—from the oxides of Antimony, 181—from Tungstic acid, 188—from Molybdic acid, 190—from Chromic acid and the oxide of Chromium, 193—from Arsenious acid and Arsenic acid, 202 and 203—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from the other acids of Sulphur, 246—from Phosphoric acid, 253—from the Phosphorous and Hypophosphorous acids, 265—from Silicic acid, 273, 283, 301—from Tantalic acid, 303—from Oxalic acid, 320—from Boracic acid, 329—from Nitric acid, 373.

LEAD. The Quantitative estimation of Lead in its compounds, is mostly the same as that of the protoxide of Lead.—Separation of Lead from Silver, ii. 117—from Mercury, 122—from Gold, 159—from Tin, 164—from Antimony, 181 and 183—from Arsenic, 203—from Tellurium, 213—from Selenium, 217 and 220—from Sulphur 226 and 238—from Chlorine, 356.

Detection of protoxide of Lead in simple soluble compounds, i. 6—in simple insoluble compounds, 13, 20—in complex soluble compounds, 22—in complex insoluble compounds, 36, 44.—Behaviour of protoxide of Lead towards reagents, 109.

Quantitative estimation of protoxide of Lead, ii. 99.—Separation of protoxide of Lead from oxide of Nickel, 100—from oxide of Cobalt, 100—from oxide of Zinc, 100—from peroxide of Iron, 100—from protoxide of Manganese, 100—from the Earths, 100—from the Alcalies, 100—from oxide of Cadmium, 103—from oxide of Bismuth, 104—from the oxides of Uranium, 107—from deutoxide of Copper, 113—from oxide of Silver, 116—from the oxides of Mercury, 128—from the oxides of Tin, 164—from Titanic acid, 169—from the oxides of Antimony, 181, 183—from Tungstic acid, 188—from Molybdic acid, 190—from Chromic acid and the oxide of Chromium, 196—from Arsenious acid and Arsenic acid, 203, 205—from oxide of Tellurium, 213—from Selenious acid, 217—from Selenic acid, 219—from Sulphuric acid, 243—from Phosphoric acid, 251 and 253—from Silicic acid, 272 and 294—from Oxalic acid, 320—from Carbonic acid, 321—from Boracic acid, 329—from Nitric acid, 371.

Behaviour of the red and brown oxides of Lead towards reagents, i. 113.

LITHIUM. Behaviour of Lithia towards reagents, i. 54.—Quantitative estimation of Lithia, ii. 9.—Separation of Lithia from Potash and Soda, 10.—The separation of Lithia from other substances is the same as the separation of Potash from the same substances. See, therefore, POTASSIUM.

MAGNESIUM. Detection of Magnesia in simple soluble compounds, i. 9.—in simple insoluble compounds, 15, 16.—in complex soluble compounds, 29—in complex insoluble compounds, 36.—Behaviour of Magnesia towards reagents, 70.

Quantitative estimation of Magnesia, ii. 23.—Separation of Magnesia from Lime, 26—from Strontian, 28—from Barytes, 28—from the Alcalies, 29—from Alumina, 31—from Glucina, 38—from Yttria, 39—from the oxides of Cerium, 40—from Zirconia, 41—from protoxide of Manganese, 46—from peroxide of Iron, 61—from oxide of Zinc, 80—from oxide of Cobalt, 89—from oxide of Nickel, 96—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 108—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Tin, 164—from Titanic acid, 172—from the oxides of Antimony, 180—from Chromic acid and the oxide of Chromium, 193—from Arsenious acid and Arsenic acid, 202 and 204—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from the other acids of Sulphur, 246—from Phosphoric acid, 257—from Phosphorous acid and Hypophosphorous acid, 265—from Silicic acid, 273, 284, 285—from Oxalic acid, 320—from Carbonic acid, 321—from Boracic acid, 329—from Nitric acid, 370.

MANGANESE. Separation of Manganese from Sulphur, ii. 223 —from Chlorine, 359.

Detection of protoxide of Manganese in simple soluble compounds, i. 8—in simple insoluble compounds, 15—in complex soluble compounds, 26—in complex insoluble compounds, 36. —Behaviour of the protoxide of Manganese towards reagents, 87.

Quantitative estimation of protoxide of Manganese, ii. 42.—Separation of protoxide of Manganese from Zirconia, 45—from the oxides of Cerium, 45—from Yttria, 45—from Glucina, 45—from Alumina, 46—from Magnesia, 46—from Lime, 48 and 49 —from Strontian, 51—from Barytes, 51—from the Alcalies, 51. —from peroxide of Iron, 55—from oxide of Zinc, 76—from oxide of Cobalt, 87—from oxide of Nickel, 96—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 108—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from oxide of Platinum, 146—from the oxides of Tin, 164—from Titanic acid, 169—from the oxides of Antimony, 181—from Tungstic acid, 188—from Molybdic acid, 190. —from Chromic acid and oxide of Chromium, 193—from Arsenious acid and Arsenic acid, 202, 203—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from Phosphoric acid, 253—from Phosphorous acid and Hypophosphorous acid, 265—from Silicic acid, 273—from Oxalic acid, 320—from Carbonic acid, 322—from Boracic acid, 329—from Nitric acid, 373.

Behaviour of deutoxide of Manganese towards reagents, i. 91. —Behaviour of peroxide of Manganese towards reagents, 93.—Quantitative estimation of the deutoxide, the intermediate brown oxide, and the peroxide of Manganese, ii. 44, 45.

MERCURY. The quantitative estimation of Mercury is mostly the same as that of peroxide of Mercury.—Separation of Mercury from non-volatile Metals, ii. 121—from Arsenic, 203—from Selenium, 217—from Sulphur, 227—from Chlorine, 357.

Detection of protoxide of Mercury in simple soluble compounds, i. 6—in simple insoluble compounds, 13, 20—in complex soluble compounds, 22—in complex insoluble compounds, 36, 42.—Behaviour of protoxide of Mercury towards reagents, 126.—Quantitative estimation of protoxide of Mercury, ii. 118 and 123.—Separation of protoxide of Mercury from oxide of

Silver, 125—from peroxide of Mercury, 130.—The separation of protoxide of Mercury from the remaining oxides is the same as that of peroxide of Mercury from the same substances.

Detection of peroxide of Mercury in simple soluble compounds, i. 6—in simple insoluble compounds, 13, 20—in complex soluble compounds, 22—in complex insoluble compounds, 36, 42.—Behaviour of peroxide of Mercury towards reagents, 129.—Quantitative estimation of peroxide of Mercury, ii. 118, 123.—Separation of peroxide of Mercury from the oxides of Uranium, 123—from oxide of Nickel, 123—from oxide of Cobalt, 123—from oxide of Zinc, 123—from peroxide of Iron, 123—from protoxide of manganese, 123—from the Earths, 123—from the Alcalies, 123—from oxide of Silver, 125—from deutoxide of Copper, 125—from protoxide of Lead, 128—from oxide of Bismuth, 129—from oxide of Cadmium, 130—from protoxide of Mercury, 130—from the oxides of Tin, 164—from the oxides of Antimony, 181—from Chromic acid and the oxide of Chromium, 192—from Arsenious acid and Arsenic acid, 203—from oxide of Tellurium, 213—from Selenious acid, 217—from Sulphuric acid, 243—from Phosphoric acid, 251 and 253—from Nitric acid, 371.

MOLYBDENUM. Quantitative estimation of Molybdic acid, ii. 189.—Separation of Molybdic acid from most oxides, 190—from the Earths and Alcalies, 190.

NICKEL. The quantitative estimation of Nickel in its compounds is like that of oxide of Nickel.—Separation of Nickel from Sulphur, ii. 223—from Phosphorus, 255.

Detection of oxide of Nickel in simple soluble compounds, i. 8—in simple insoluble compounds, 14—in complex soluble compounds, 26—in complex insoluble compounds, 36.—Behaviour of oxide of Nickel towards reagents, 99.—Quantitative estimation of oxide of Nickel, ii. 91.—Separation of oxide of Nickel from oxide of Cobalt, 92—from oxide of Zinc, 94—from peroxide of Iron, 95—from protoxide of Manganese, 96—from Alumina, 96—from Magnesia, 96—from Lime, 96—from Strontian, 97—from Barytes, 97—from the Alcalies, 97—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 107—from deutoxide of copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Tin, 164—from the oxides of Antimony, 181, 183—from Chromic acid and the oxide of Chromium, 193—from Arsenious acid and Arsenic acid, 202—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from Phosphoric acid, 254.

Behaviour of peroxide of Nickel towards reagents, i. 101.

NITROGEN. Quantitative estimation of Nitrogen, ii. 369.—Separation of Nitrogen from Oxygen, 375—from Chlorine, 376—from Iodine, 376—from Carbon, 376.—Separation of Nitrogen gas from Oxygen gas: analysis of Atmospheric Air, 391—from Oxygen gas and Hydrogen gas, 392—from carburetted Hydrogen gas, 410.—Analysis of substances which contain Nitrogen, by means of Chlorate of Potash, 415—by means of oxide of Copper, 420.

Detection of Nitric acid in simple soluble compounds, i. 12—in simple insoluble compounds, 17—in complex soluble compounds, 33—in complex insoluble compounds, 39.—Behaviour of Nitric acid towards reagents, 158.—Quantitative estimation of Nitric acid, ii. 369.—Separation of Nitric acid from metallic oxides, 370—from Barytes and Strontian, 373—from the Alcalies, 374.

Behaviour of Nitrous and Hyponitrous acids towards reagents, i. 161.

Quantitative estimation of Cyanogen in Cyanurets, ii. 376.—Separation of Cyanogen from metals, 376.—Analysis of the simple Cyanurets, 377—of the double Cyanurets, 377.—Analysis of the Cyanites and Cyanates, 379.—Quantitative estimation of Hydrocyanic acid, 407.

Detection of Ammonia in simple soluble compounds, i. 10—in complex soluble compounds, 30.—Behaviour of Ammonia towards reagents, 57.—Quantitative estimation of Ammonia in ammoniacal salts, ii. 400.—Estimation of Water in ammoniacal salts, 401.—Quantitative estimation of gaseous Ammonia, 404.—Separation of gaseous Ammonia from other gases, 406.

OSMIUM. Quantitative estimation of Osmium, ii. 138.—Separation of Osmium from other Metals, 139—from Iridium, 139—from Platinum, Rhodium, and Palladium, 147.—Test for Osmium, 143.

PALLADIUM. Quantitative estimation of Palladium, ii. 135.—

Separation of Palladium from most other metals, 135—from Copper, 135—from Alcaline metals, 136—from Platinum, Rhodium, Iridium, and Osmium, 147.

PHOSPHORUS. Quantitative estimation of metallic Phosphurets, ii. 255.—Separation of Phosphorus from Carbon, 309—from Iron, 316—from Chlorine, 349, 352—from Hydrogen, 412.

Quantitative estimation of Hypophosphorous acid, ii. 249—of the Hypophosphates, 265.—Separation of Hypophosphorous acid from Phosphoric acid, 267.

Quantitative estimation of Phosphorous acid, ii. 249—of the Phosphites, 265.—Separation of Phosphorous acid from Phosphoric acid, 267.

Detection of Phosphoric acid in simple soluble compounds, i. 10—in simple insoluble compounds, 19—in complex soluble compounds, 31—in complex insoluble compounds, 39, 44.—Behaviour of Phosphoric acid towards reagents, 168.

Quantitative estimation of Phosphoric acid, ii. 249.—Separation of Phosphoric acid from Sulphuric acid, 250 and 264—from Arsenious acid and Arsenic acid, 251—from oxide of Cadmium, 251, 253—from protoxide of Lead, 251 and 253—from oxide of Bismuth, 251, 253—from deutoxide of Copper, 251, 253—from oxide of Silver, 251 and 252—from peroxide of Mercury, 251, 253—from the oxides of Tin, 251—from the oxides of Antimony, 251—from oxide of Cobalt, 253—from oxide of Zinc, 253—from peroxide of Iron, 253—from protoxide of Manganese, 253—from Chromic acid and the oxide of Chromium, 254—from the oxides of Uranium, 254—from oxide of Nickel, 254—from Yttria, 256—from Alumina, 256—from Magnesia, 257—from Lime, 258—from Strontian, 258—from Barytes, 258—from Potash, 258—from Soda, 258—from Lithia, 259—from Phosphorous acid and Hypophosphorous acid, 267—from Silicic acid, 294—from Fluorides, 346—from Chlorides, 361.

PLATINUM. Behaviour of oxide and chloride of Platinum towards reagents, i. 136.—Quantitative estimation of Platinum, ii. 144.—Separation of Platinum from Manganese, Iron, Cobalt, Nickel, Copper, Mercury, &c. 146—from Osmium, Iridium, Palladium, and Rhodium, 147—from Gold, 161—from Tin, 164—from Antimony, 183—from Arsenic, 206—from Sulphur, 227.

POTASSIUM. Separation of Potassium from Sulphur, ii. 228—, from Chlorine, 349.—Detection of Potash in simple soluble compounds, i. 10—in complex soluble compounds, 29.—Behaviour of Potash towards reagents, 46.

Quantitative estimation of Potash, ii. 5.—Separation of Potash from Soda, 8—from Lithia, 10—from Soda and Lithia, 12—from Barytes, 13—from Strontian, 15—from Lime, 22—from Magnesia, 29—from Alumina, 36—from Glucina, 39—from Yttria, 39—from the oxides of Cerium, 40—from Zirconia, 41—from protoxide of Manganese, 51—from peroxide of Iron, 61—from oxide of Zinc, 82—from oxide of Cobalt, 90—from oxide of Nickel, 97—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 108—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from peroxide of Rhodium, 134—from peroxide of Palladium, 136—from oxide of Platinum, 145—from the oxides of Tin, 164—from Titanic acid, 173—from the oxides of Antimony, 180—from Tungstic acid, 188—from Molybdic acid, 190—from Chromic acid and the oxide of Chromium, 193—from Arsenious acid and Arsenic acid, 202 and 204—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from the other acids of Sulphur, 246—from Phosphoric acid, 258—from Phosphorous and Hypophosphorous acids, 265—from Silicic acid, in compounds which are decomposable by acids, 273—from Silicic acid, in compounds which are not decomposable by acids, 280—from Oxalic acid, 320—from Carbonic acid, 325—from Boracic acid, 329—from Chlorous acid, 363—from Nitric acid, 374.

RHODIUM. Quantitative estimation of Rhodium, ii. 131.—Separation of Rhodium from many other metals, 131—from Copper, 133—from Iron, 133—from alcaline Metals, 134—from Platinum, Palladium, Iridium, and Osmium, 147.

SELENIUM. The quantitative estimation of Selenium is mostly like that of Selenious acid.—Separation of Selenium from Manganese, ii. 217—from Iron, 217—from Zinc, 217—from Cobalt, 217 and 220—from Nickel, 217 and 220—from Cadmium, 217—from Lead, 217 and 220—from Bismuth, 217—from Copper, 217 and 220—from Silver, 217 and 220—from Mercury, 217—from Tellurium, 222—from Arsenic, 222—from Antimony, 222

—from Sulphur, 228—from Chlorine, 349, 352, 354—from Hydrogen, 415.

Quantitative estimation of Selenious acid, ii. 215.—Separation of Selenious acid from the Alcalies, 216—from the Earths, 216—from protoxide of Manganese, 216—from peroxide of Iron, 216—from oxide of Zinc, 216—from oxide of Cobalt, 216—from oxide of Nickel, 216—from oxide of Cadmium, 217—from protoxide of Lead, 217—from oxide of Bismuth, 217—from deutoxide of Copper, 217—from oxide of Silver, 217—from peroxide of Mercury, 217—from oxide of Tellurium, 222—from Arsenious acid and Arsenic acid, 222—from the oxides of Antimony, 222—from the oxides of Tin, 222—from Selenic acid, 222—from Phosphoric acid, 251.

Quantitative estimation of Selenic acid, ii. 215.—Separation of Selenic acid from other substances, 217 and 219—from Selenious acid, 222—from oxide of Tellurium, 222—from the oxides and acids of Antimony and Arsenic, 222.

SILICIUM. Separation of Silicium from Iron, ii. 317—from Fluorine, 336.

Behaviour of Silicic acid towards reagents, i. 182.—Quantitative estimation of Silicic acid, ii. 269.—Progress of the Analysis of the Silicates which are decomposed by Acids, 269 and 273.—Separation of Silicic acid from protoxide of Lead, 272—from oxide of Silver, 272—from Alumina, 273—from peroxide of Iron, 273—from Lime, 273—from Magnesia, 273—from protoxide of Manganese, 273—from the Alcalies, 273.—Progress of the Analysis of Silicates which are indecomposable by Acids, 274, 291.—Separation of Silicic acid from Alcalies in such compounds, 280.—Separation of Silicic acid from Phosphoric acid, 294—from Sulphuric acid, 296—from Sulphur, 297—from oxide of Chromium, 297—from Titanic acid, 298—from peroxide of Tin, 300—from deutoxide of Copper, 301—from peroxide and protoxide of Iron, 301—from Tantalic acid, 306—from Carbon, 308—from Boracic acid, 330—from Fluorides, 338—from Chlorides, 360.

List of the Minerals which are decomposable by Acids, i. 186.—List of the Minerals which are decomposable by fusion with Alcaline Carbonates, 188.—List of the Minerals which require fusion with Caustic Potash for their decomposition, 189.

SILVER. The quantitative estimation of Silver in its compounds is mostly like that of oxide of Silver.—Separation of Silver from Copper, ii. 117—from Lead, 117—from Mercury, 122—from Gold, 159—from Tin, 164—from Antimony, 181 and 183—from Arsenic, 203—from Tellurium, 214—from Selenium, 217 and 220—from Sulphur, 227, 238, 241—from Chlorine, 356.

Detection of oxide of Silver in simple soluble compounds, i. 6—in simple insoluble compounds, 13, 20—in complex soluble compounds, 22—in complex insoluble compounds, 36, 44.—Behaviour of oxide of Silver towards reagents, 123.—Quantitative estimation of oxide of Silver, ii. 115.—Separation of oxide of Silver from protoxide of Lead, 116—from most other Oxides, as well as from Earths and Alcalies, 117—from the oxides of Mercury, 125—from the oxides of Tin, 164—from the oxides of Antimony, 181, 183—from Chromic acid, 196—from Arsenious acid and Arsenic acid, 203—from oxide of Tellurium, 213—from Selenious acid and Selenic acid, 217—from Sulphuric acid, 243—from Phosphoric acid, 251, 253.

SODIUM. Detection of Soda in simple soluble compounds, i. 10—in complex soluble compounds, 29.—Behaviour of Soda towards reagents, 51.—Discrimination of Soda from Potash, 10 and 29.

Quantitative estimation of Soda, ii. 8.—The separation of Soda from other substances is the same as the separation of Potash from the same substances.

STRONTIUM. Detection of Strontian in simple soluble compounds, i. 9—in simple insoluble compounds, 15, 16, and 20—in complex soluble compounds, 28—in complex insoluble compounds, 36 and 44.—Behaviour of Strontian towards reagents, 63.

Quantitative estimation of Strontian, ii. 13.—Separation of Strontian from Barytes, 14—from the Alcalies, 15—from Lime, 18—from Magnesia, 28—from Alumina, 35—from Glucina, 39—from Yttria, 39—from the oxides of Cerium, 40—from Zirconia, 41—from protoxide of Manganese, 51—from peroxide of Iron, 61—from oxide of Zinc, 81—from oxide of Cobalt, 90——from oxide of Nickel, 97—from oxide of Cadmium, 97—from protoxide of Lead, 100—from oxide of Bismuth, 105—from the oxides of Uranium, 108—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Tin, 164—from Titanic acid, 173—from the oxides of

Antimony, 180—from Chromic acid and the oxide of Chromium, 193—from Arsenious acid and Arsenic acid, 202, 204, and 205—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from the other acids of Sulphur, 246—from Phosphoric acid, 258—from Phosphorous acid and Hypophosphorous acid, 265—from Oxalic acid, 320—from Carbonic acid, 325—from Boracic acid, 329—from Nitric acid, 373.

SULPHUR. Detection of Sulphur in simple soluble compounds, i. 10—in simple insoluble compounds, 17, 18, 20—in complex soluble compounds, 31—in complex insoluble compounds, 38 and 42.—Behaviour of metallic Sulphurets towards reagents, 200.

Quantitative estimation of Sulphur, ii. 223.—Separation of Sulphur from Manganese, 223 and 233—from Iron, 223 and 237—from Zinc, 223 and 238—from Cobalt, 223 and 233—from Nickel, 223 and 233—from Cadmium, 223—from Copper, 223 and 233—from Lead, 226 and 238—from Bismuth, 226, 241—from Silver, 227, 238, 241—from Mercury, 227—from Gold, 227—from Platinum, 227—from Tin, 227—from Titanium, 227—from Antimony, 228, 236, 237, 238, 241—from Arsenic, 228 and 237—from Selenium, 228—from Tellurium, 228—from the Metals of the Alcalies and Earths, 228—from Silicates, 297—from Carbon, 309, 311—from Carbon and Iron, 315—from Chlorine, 349, 355—from Hydrogen, 413.

Quantitative estimation of Hyposulphurous acid and the Hyposulphites, ii. 246.

Behaviour of Sulphurous acid towards reagents, i. 155.—Quantitative estimation of Sulphurous acid and the Sulphites, ii. 246.—Separation of Sulphurous acid from Sulphuric acid, 248.

Quantitative estimation of Hyposulphuric acid and the Hyposulphates, ii. 246.—Separation of Hyposulphuric acid from Sulphuric acid, 247.

Detection of Sulphuric acid in simple soluble compounds, i. 11—in simple insoluble compounds, 19, 20—in complex soluble compounds, 31—in complex insoluble compounds, 38, 43.—Behaviour of Sulphuric acid towards reagents, 152.

Quantitative estimation of Sulphuric acid, ii. 243.—Separation of Sulphuric acid from Bases in soluble compounds, 243—in insoluble compounds, 243—from the Sulphovinic acid, 247—from Phosphoric acid, 250, 264—from Silicic acid, 296—from Fluorides, 348—from Chromic acid, 245.

TANTALUM. Quantitative estimation of Tantalic acid, ii. 302.—Separation of Tantalic acid from most Oxides, 303—from peroxide of Tin, 303—from peroxide of Iron, 303—from Tungstic acid, 303—from Yttria, 305—from peroxide of Uranium, 305—from Silicic acid, 306.

TELLURIUM. The quantitative estimation of Tellurium is mostly effected like that of oxide of Tellurium.—Separation of Tellurium from most Metals, ii. 212 and 214—from Gold, 214—from Tin, 214—from Antimony, 214—from Arsenic, 214—from Selenium, 222—from Sulphur, 228—from Hydrogen, 415.

Quantitative estimation of oxide of Tellurium, ii. 212.—Separation of oxide of Tellurium from the Alcalies, 212—from the Earths, 212—from protoxide of Manganese, 212—from peroxide of Iron, 212—from oxide of Zinc, 212—from oxide of Cobalt, 212—from oxide of Nickel, 212—from the oxides of Uranium, 212—from oxide of Cadmium, 213—from protoxide of Lead, 213—from oxide of Bismuth, 213—from deutoxide of Copper, 213—from oxide of Silver, 213—from peroxide of Mercury, 213—from Selenious acid, 222—from Selenic acid, 222—from Sulphuric acid, 243—from Phosphoric acid, 251.

THORINUM. Behaviour of Thorina towards reagents, i. 79.

TIN. The quantitative estimation of Tin in its compounds is mostly the same as that of the oxides of Tin.—Separation of Tin from most other Metals, ii. 164—from Gold, 164—from Platinum, 164—from Antimony, 185—from Arsenic, 207—from Tellurium, 214—from Sulphur, 227, 233—from Chlorine, 349, 352.

Detection of protoxide of Tin in simple soluble compounds, i. 8—in simple insoluble compounds, 13—in complex soluble compounds, 22—in complex insoluble compounds, 35.—Behaviour of protoxide of Tin towards reagents, 142.—Quantitative estimation of protoxide of Tin, ii. 162.—Separation of protoxide of Tin from peroxide of Tin, 165.—The separation from other substances is similar to that of the peroxide from the same substances.

Detection of peroxide of Tin in simple soluble compounds,

i. 7—in simple insoluble compounds, 13—in complex soluble compounds, 22—in complex insoluble compounds, 35.—Behaviour of peroxide of Tin towards reagents, 144.

Quantitative estimation of peroxide of Tin, ii. 162.—Separation of protoxide of Tin from oxide of Gold, 164—from oxide of Platinum, 164—from peroxide of Mercury, 164—from oxide of Silver, 164—from deutoxide of Copper, 164—from oxide of Bismuth, 164—from protoxide of Lead, 164—from oxide of Cadmium, 164—from oxide of Nickel, 164—from oxide of Cobalt, 164—from oxide of Zinc, 164—from peroxide of Iron, 164—from protoxide of Manganese, 164—from the Earths, 164—from the Alcalies, 164—from protoxide of Tin, 164—from the oxides of Antimony, 185—from Arsenious acid and Arsenic acid, 207—from Sulphuric acid, 243—from Phosphoric acid, 251—from Silicic acid, 300—from Tantalic acid, 303.

TITANIUM. Separation of Titanium from Sulphur, ii. 227—from Chlorine, 349, 353.—Quantitative estimation of Titanic acid, ii. 167.—Separation of Titanic acid from the oxides of Tin, 169—from the oxides of Mercury, 169—from oxide of Silver, 169—from deutoxide of Copper, 169—from oxide of Bismuth, 169—from protoxide of Lead, 169—from oxide of Cadmium, 169—from oxide of Cobalt, 169—from oxide of Zinc, 169—from protoxide of Manganese, 169—from the oxides of Iron, 170—from protoxide of Iron, 171—from peroxide of Iron, 171—from Zirconia, 171—from the oxides of Cerium, 172—from Yttria, 172—from Magnesia, 172—from Lime, 172—from Strontian, 173—from Barytes, 173—from the Alcalies, 173—from the oxides of Antimony, 181—from Arsenious acid and Arsenic acid, 202—from Sulphuric acid, 243—from Silicic acid, 298.

TUNGSTENUM. Quantitative estimation of Tungstic acid, ii. 187.—Separation of Tungstic acid from most other Oxides, 188—from the Alcalies and Earths, 188—from Tantalic acid, 313.

URANIUM. Quantitative estimation of the oxides of Uranium, ii. 106.—Separation of the oxides of Uranium from oxide of Bismuth, 107—from protoxide of Lead, 107—from oxide of Cadmium, 107—from oxide of Nickel, 107—from oxide of Cobalt, 107—from oxide of Zinc, 107—from peroxide of Iron, 108

247—from Phosphoric acid, 250, 264—from Silicic acid, 296—from Fluorides, 348—from Chromic acid, 245.

TANTALUM. Quantitative estimation of Tantalic acid, ii. 302. —Separation of Tantalic acid from most Oxides, 303—from peroxide of Tin, 303—from peroxide of Iron, 303—from Tungstic acid, 303—from Yttria, 305—from peroxide of Uranium, 305—from Silicic acid, 306.

TELLURIUM. The quantitative estimation of Tellurium is mostly effected like that of oxide of Tellurium.—Separation of Tellurium from most Metals, ii. 212 and 214—from Gold, 214—from Tin, 214—from Antimony, 214—from Arsenic, 214—from Selenium, 222—from Sulphur, 228—from Hydrogen, 415.

Quantitative estimation of oxide of Tellurium, ii. 212.—Separation of oxide of Tellurium from the Alcalies, 212—from the Earths, 212—from protoxide of Manganese, 212—from peroxide of Iron, 212—from oxide of Zinc, 212—from oxide of Cobalt, 212—from oxide of Nickel, 212—from the oxides of Uranium, 212—from oxide of Cadmium, 213—from protoxide of Lead, 213—from oxide of Bismuth, 213—from deutoxide of Copper, 213—from oxide of Silver, 213—from peroxide of Mercury, 213—from Selenious acid, 222—from Selenic acid, 222—from Sulphuric acid, 243—from Phosphoric acid, 251.

THORINUM. Behaviour of Thorina towards reagents, i. 79.

TIN. The quantitative estimation of Tin in its compounds is mostly the same as that of the oxides of Tin.—Separation of Tin from most other Metals, ii. 164—from Gold, 164—from Platinum, 164—from Antimony, 185—from Arsenic, 207—from Tellurium, 214—from Sulphur, 227, 233—from Chlorine, 349, 352.

Detection of protoxide of Tin in simple soluble compounds, i. 8—in simple insoluble compounds, 13—in complex soluble compounds, 22—in complex insoluble compounds, 35.—Behaviour of protoxide of Tin towards reagents, 142.—Quantitative estimation of protoxide of Tin, ii. 162.—Separation of protoxide of Tin from peroxide of Tin, 165.—The separation from other substances is similar to that of the peroxide from the same substances.

Detection of peroxide of Tin in simple soluble compounds, Chromium, 193—from the oxides of Arsenic, 202 and 203—from oxide of Tellurium, 212—from Selenious acid, 216—from Selenic acid, 217—from Sulphuric acid, 243—from the other acids of Sulphur, 246—from Phosphoric acid, 253—from Phosphorous acid and Hypophosphorous acid, 265—from Nitric acid, 373.

ZIRCONIA. Behaviour of Zirconia towards reagents, i. 85.—Quantitative estimation of Zirconia, ii. 41.—Separation of Zirconia from the oxides of Cerium, 41—from Yttria, 41—from Glucina, 41—from Alumina, 41—from Magnesia, 41—from Lime, 41—from Strontian, 41—from Barytes, 41—from the Alcalies, 41—from protoxide of Manganese, 45—from peroxide of Iron, 58—from oxide of Zinc, 80—from deutoxide of Copper, 113—from oxide of Silver, 116—from peroxide of Mercury, 123—from the oxides of Tin, 164—from Titanic acid, 171—from Sulphuric acid, 243.

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